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PHYSICAL REVIEW

THE MAGNITUDE OF THE K-ABSORPTION DISCONTINUITY

By F. K. Richtmyer*

Abstract

Mass absorption coefficients for wave-lengths on both sides of the K limit. (1) *Experimental results for six metals.* Using a water cooled Mo tube, absorption measurements were made for a sufficient range of wave-lengths in each case to determine the constants in the equations for the mass absorption coefficients above and below the K absorption discontinuity. $\mu_K/\rho = K_K\lambda^3 + \sigma/\rho$; $\mu_L/\rho = K_K\lambda^3 + \sigma/\rho$, in which σ/ρ is the scattering coefficient, with a value of 1 or less. λ is in angstrom units. τ_a is the atomic absorption coefficient at the K limit, corrected for scattering.

	Mo(42)	Ag(47)	Sn(50)	W(74)	Au(79)	Pb(82)
$k_K =$	375	545	595	1870	2230	2570
$k_L =$	50	70	90	330	395	476
$k_K/k_L =$	7.5	7.8	6.6	5.65	5.65	5.40
$\tau_a(10^{-21}) =$	13.3	11.0	8.90	3.19	2.57	2.37

(2) *Comparison with theories.* $(k_K/k_L - 1)$ is the ratio of the number of photoelectrons originating in the K and L levels for x-rays just shorter than the K limit. It is shown that the theories of Thomson, of Compton, and of de Broglie lead to the same values of k_K/k_L, which increase with decreasing atomic number in agreement with experiment except that they are about twice too large. Kramers' formula gives a value which does not vary with N and which agrees well with the experimental values for Mo to Pb, but it applies only to a single electron around the nucleus. A formula modified by use of Bohr's theory of energy levels to remove this restriction gives values nearly three times too large. No present theory, then, is supported by these experimental results.

Introduction

SEVERAL attempts[1,2,3,4] have been made to obtain, on theoretical grounds, the equation

$$\tau_a = C N^4 \lambda^3 \qquad (1)$$

which has been found by experiment to represent the relation between the atomic fluorescent absorption coefficient τ_a for x-rays of wave-length λ absorbed by a substance of atomic number N. C is a constant for all

* This work has been made possible by a grant to the writer, from the Heckscher Research Council of Cornell University.

[1] J. J. Thomson, Conduction of Electricity through Gases, 2d. Ed., p. 321.

[2] L. de Broglie, Journ. de Phys. et Rad. **3**, 33 (1922).

[3] A. H. Compton, Nat. Res. Council, Bul. **20**, 37 (1922).

[4] H. A. Kramers, Phil. Mag. **46**, 836 (1923).

M. S.

elements on the short wave-length side of the K absorption limit, and has a numerical value[5] of 22.4×10^{-27}, λ being expressed in angstrom units. At the K limit the value of C decreases abruptly. If we put

$$R_{\mathrm{L}}^{\mathrm{K}} = \frac{C_{\mathrm{K,L}\ldots.}}{C_{\mathrm{L}\ldots..}} \tag{2}$$

where $C_{\mathrm{K,L}\ldots}$ is the value of C on the short wave-length side of the K limit and $C_{\mathrm{L}\ldots}$ that on the long wave-length side, then the ratio $R_{\mathrm{L}}^{\mathrm{K}}$ of the two values of C depends on the atomic number of the absorber, being less for elements of higher atomic number. For example, for elements in the neighborhood of Ag $R_{\mathrm{L}}^{\mathrm{K}}$ is about 8. For elements in the neighborhood of Pt it is about 5.5.

The several theoretical formulas above referred to, although obtained on the basis of widely different considerations, agree with experiments in assigning 4 and 3 as the exponents of N and λ respectively in Eq. (1). There is a disagreement, however, with experiment, in respect to not only the magnitude of $R_{\mathrm{L}}^{\mathrm{K}}$ but also its variation with atomic number. The extent to which any theoretical formula agrees with experiment in predicting the correct value of $R_{\mathrm{L}}^{\mathrm{K}}$ is therefore a more discriminating test of the correctness of the formula than are the coefficient of N and λ.

A knowledge of the precise value of $R_{\mathrm{L}}^{\mathrm{K}}$ is of prime importance in connection with further extensions of our present very incomplete "picture" of the interaction between radiation and matter. So far as it goes this picture is quite precise with regard to the sequence of the main events in the (fluorescent) absorption of x-rays. Thus, if a monochromatic x-ray beam of frequency ν and of quantum energy $h\nu$ strikes an absorber the frequency of whose K absorption limit ν_{K} is less than ν, the first process is the photo-electric expulsion of electrons from the several electron levels[6] in the atom according to the well known equation

$$h\nu = W + h\nu_{\mathrm{K,L,M}\ldots} \tag{3}$$

where $h\nu_{\mathrm{K,L,M}\ldots}$ represents in turn the work necessary to remove electrons from the K, L, M . . . levels respectively and W is the residual kinetic energy of the photo-electron originating in the K, L, M. . . level. The vacant place in the atom is then filled by an electron from an outside level, or from infinity, and the K, L, M. . . fluorescent radiation results. It is to be remembered, however, that, irrespective either of what ultimately becomes of the energy given to the electron or whether a K, L or M electron is expelled, *each photo-electron removes from the incident beam*

[5] F. K. Richtmyer and F. W. Warburton, Phys. Rev. **22,** 539 (1923).

[6] See, for example, the beautiful experiments of Robinson, Proc. Roy. Soc. **104,** 455 (Nov. 1923).

an amount of energy $h\nu$. By dividing by $h\nu$ the total amount of energy removed by the absorber in this fluorescent process, the total *number* of photo-electrons produced under given conditions, may be obtained. We have at present no way of measuring with acceptable precision the actual magnitude of this absorbed energy, but by comparing the fluorescent absorption coefficient on the short wave-length side of the K absorption limit with that on the long wave-length side, it is possible to get the ratio of the total number of (K+L+M . . .) photo-electrons to the total number of (L+M. . .) photo-electrons. Thus

$$R_L^K = \frac{\text{total number of K+L+M+ . . . photo-electrons}}{\text{total number of L+M+. . . photo-electrons}} \qquad (4)$$

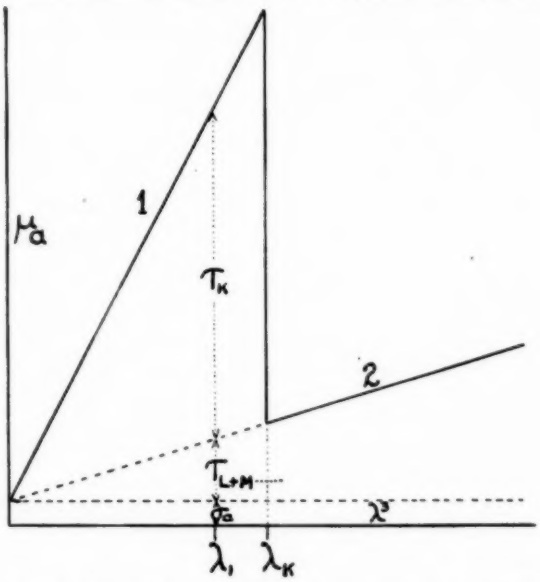

Fig. 1. Variation of the atomic absorption coefficient with the cube of the wave-length.

This relation is shown graphically in Fig. 1, which represents diagrammatically,[7] to approximate scale, the linear relation between the atomic absorption coefficient μ_a and the cube of the wave-length on both sides of the absorption limit. Thus, if radiation of wave-length $\lambda_1 < \lambda_K$ falls on the absorber, we may regard the atomic absorption coefficient at that wave-length as being made up of several parts: (1) a part τ_K due to the energy removed from the beam by the expulsion of K photo-electrons; (2) a part $\tau_{L+M+\ldots}$ due to the expulsion of L+M+. . . photo-electrons; and (3) a part σ_a due to the energy removed by scattering. Although σ_a and its variation with wave-length are of very great theoretical signifi-

[7] F. K. Richtmyer, loc. cit. 10, p. 27.

cance, it is responsible for only a small proportion of the energy removed from the incident beam, especially in those elements and for those wavelengths for which R_L^K is known. Hence to a first approximation σ_a may be considered as constant and equal to the intercept on the μ_a axis, of the absorption curves on both sides of the K limit. Accordingly it is obvious that the ratio

$$(\tau_K+\tau_{L+M+}\ldots)/(\tau_{L+M+}\ldots) = R_K^L \qquad (5)$$

gives the relative number of the several "kinds" of photo-electrons, and hence the relative probabilities of the expulsion of electrons from the several energy levels within the atom. It is this probability which has been computed by the several writers[1,2,3,4] and which it is desired to compare with experiment.

Data on the K Discontinuity

The experimental data on the magnitude of the K absorption discontinuity are very meager. Discarding, as of comparatively little value, the measurements with heterogeneous radiation, there are collected in columns 3, 4, and 5 of Table I data obtained by use of monochromatic radiation by Wingardh,[8] Allen,[9] and the writer.[10] At the December 1923 meeting of the American Physical Society, Mr. F. W. Warburton[11] in collaboration with the writer presented, in brief form, some data on the K discontinuities for several elements. The data were not regarded as very satisfactory, and publication of the results in full was delayed until further measurements could be made. Other investigations have pre-

Table I

Element	Atomic Number	Values of R_L^K			
		Wingardh[8]	Allen[9]	Richtmyer[10]	Richtmyer and Warburton[11]
Mo	42			8.7	7.5
Ag	47	8.0*	7.1*	7.3	7.8
Sn	50		8.9†		6.6
W	74		6.0		5.65
Pt	78		5.3		
Au	79		5.0		5.65
Pb	82		4.5		5.40
Bi	83		4.1		

* Computed from data given in reference.

† Computed by combining data given by Allen (loc. cit.[9]), with data given by Bragg and Pierce (Phil. Mag. **28**, 626, 1914).

[8] K. A. Wingardh, Dissertation, Lund (1923).

[9] S. J. M. Allen, Phys. Rev. **24**, 1 (July 1924).

[10] F. K. Richtmyer, Phys. Rev. **18**, 13 (July 1921).

[11] F. W. Warburton and F. K. Richtmyer, Phys. Rev. **23**, 291 (Feb. 1924).

vented further progress on the work; so in this paper are presented the data of Warburton and Richtmyer, with some minor corrections.

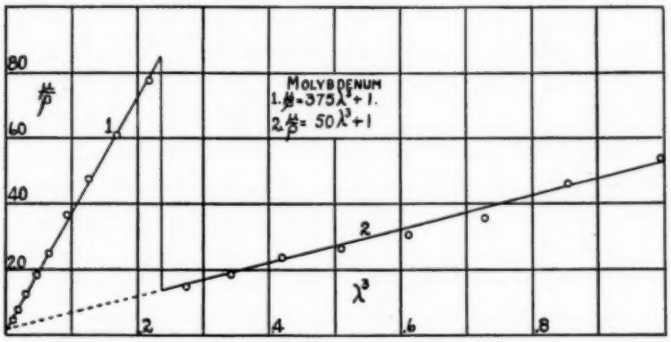

Fig. 2. Variation of the mass absorption coefficient of molybdenum with the cube of the wave-length.

The method of measuring coefficients of absorption of x-rays is too well known to require comment. The apparatus used for the present investigation has been previously described.[12] For obtaining sufficient energy at

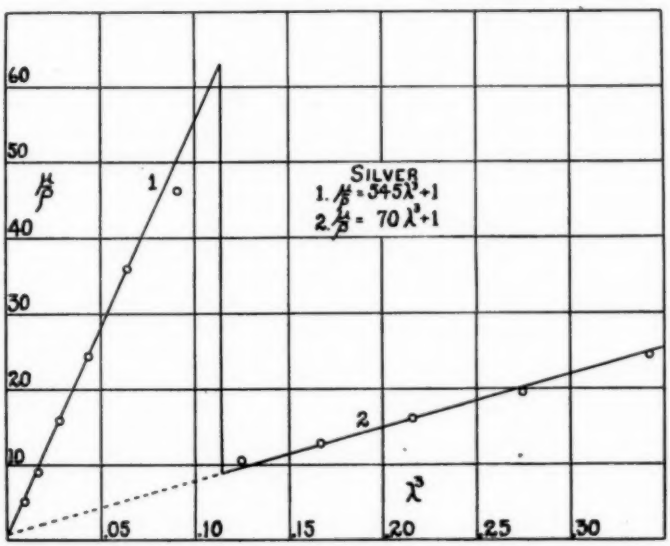

Fig. 3. Variation of the mass absorption coefficient of silver with the cube of the wave-length.

the longer wave-lengths herein reported, a water-cooled molybdenum tube was used. The writer is indebted to Dr. W. D. Collidge of the General Electric Company, for the use of this tube.

[12] F. K. Richtmyer and F. W. Warburton, Phys. Rev. **22**, 539 (1923).

Observations were made through the K absorption limits of Mo, Ag, Sn, W, Au, and Pb. The data are shown in graphical form in Figs. 2-7,

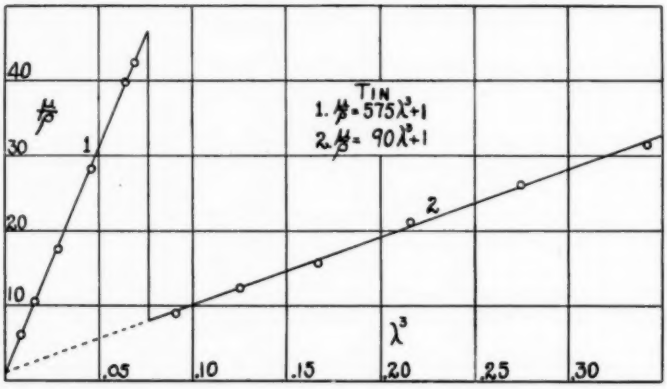

Fig. 4. Variation of the mass absorption coefficient of tin with the cube of the wave-length.

in which the mass absorption coefficients for the several elements are plotted as functions of the cube of the wave-length. In these graphs the

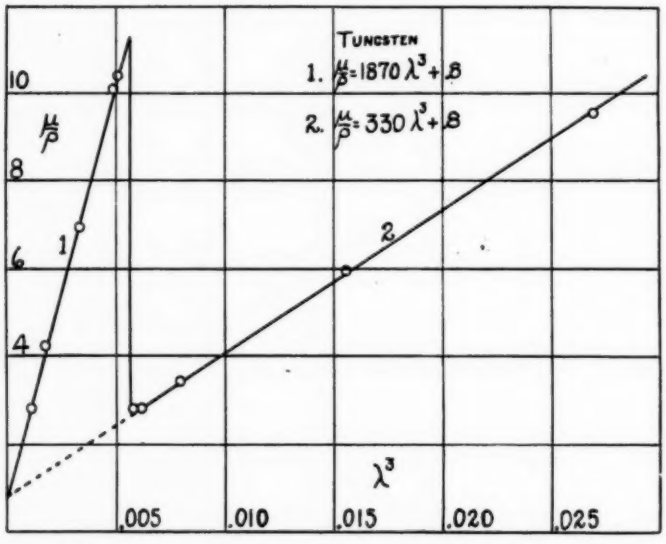

Fig. 5. Variation of the mass absorption coefficient of tungsten with the cube of the wave-length.

K_ϵ absorption discontinuity is represented by a vertical line, since, as has been recently shown by the writer,[13] the K discontinuity for silver shows no measurable structure and is sharp to at least .0001A. Since, to a very

[13] F. K. Richtmyer, Phys. Rev. **26**, 724 (Dec. 1925).

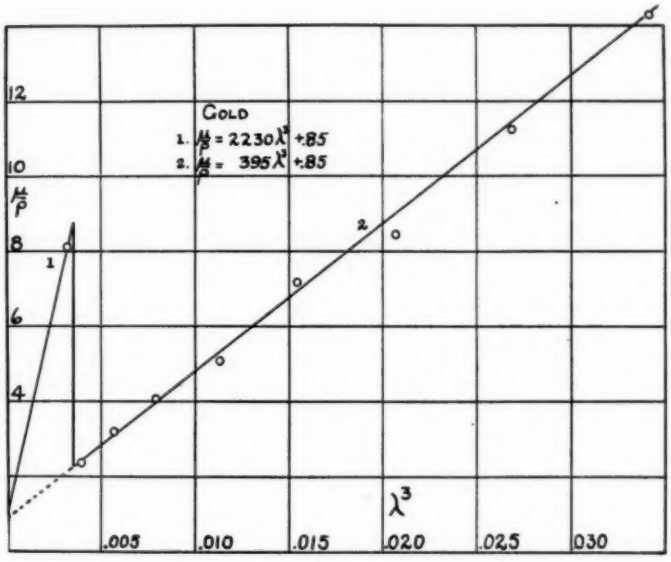

Fig. 6. Variation of the mass absorption coefficient of gold with the cube of the wave-length.

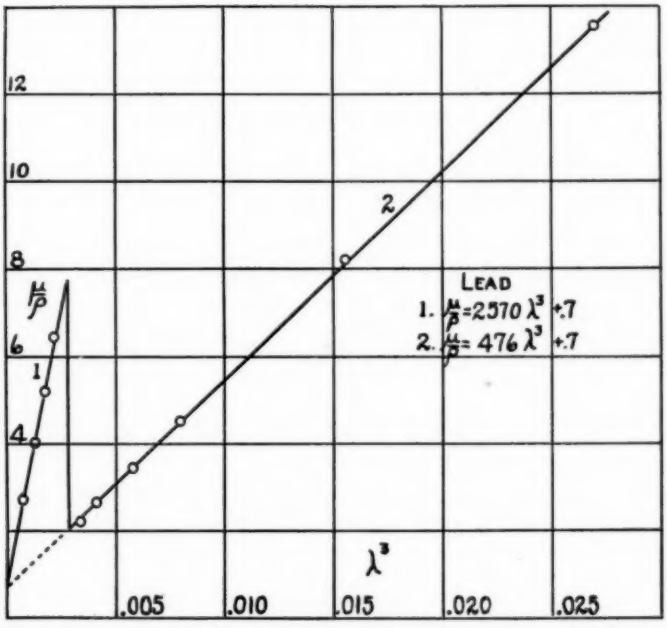

Fig. 7. Variation of the mass absorption coefficient of lead with the cube of the wave-length.

close approximation at least, the graphs, both above and below the K limit are straight lines, and have nearly, if not quite, identical intercepts on the μ/ρ axis, it is obvious that the values of R_L^K are given by the ratios of the slope of the graph on the short wave-length side of the limit to that on the long wave-length side. These slopes are collected in columns 2 and 3 of Table II, the values k_K and k_L being the values in the equations

$$\mu_K/\rho = k_K\lambda^3 + \sigma/\rho \tag{6}$$

$$\mu_L/\rho = k_L\lambda^3 + \sigma/\rho \tag{7}$$

TABLE II

The values of k_K and k_L are the slopes of the curves in figs. 2-7; $(\mu/\rho)_{max}$ is the maximum value reached by μ/ρ just at the short wave-length side of the K limit; $(\tau/\rho)_{max}$ is obtained by subtracting from $(\mu/\rho)_{max}$ the intercept on the μ/ρ axis; n gives the number of atoms per gram; $(\tau a)_{max}$ is obtained by dividing $(\tau/\rho)_{max}$ by n; R_L^K is the ratio k_K/k_L.

Element		k_K	k_L	$(\mu/\rho)_{max}$	$(\tau/\rho)_{max}$	n	$(\tau a)_{max}$	R_L^K
Mo	42	375	50	85.0	84.0	6.31×10^{21}	13.3×10^{-21}	7.5
Ag	47	545	70	63.0	62.0	5.61	11.0	7.8
Sn	50	595	90	46.5	45.5	5.11	8.90	6.6
W	74	1870	330	11.3	10.5	3.29	3.19	5.55
Aw	79	2230	395	8.8	7.9	3.07	2.57	5.65
Pb	82	2570	476	7.8	6.9	2.91	2.37	5.4

μ_K and k_K refer to the short wave-length side of the limit; μ_L and k_L to the long wave-length side. From what has been said before it is evident that the ratio R_L^K is given by

$$R_L^K = k_K/k_L$$

These ratios are tabulated in column 8 of Table II and also for comparison with results of others, in column 6 of Table I.

A glance at Table I makes it obvious that the data warrant only the general conclusions that there is agreement on the order of magnitude of the discontinuity and that the values of R_L^K range from around 5.5* for the heavier elements to 7.5 or 8 for elements in the neighborhood of silver.

* A careful examination of Allen's data makes it seem probable that the values given by him for the heavier elements are too low. This statement is based on the circumstance that, beginning with tungsten, Allen's values of μ/ρ on the short wave-length side of the K limit *decrease*, at any given wave-length, with *increasing* atomic number, a result quite in opposition to data obtained by other investigators. Allen's curves reveal the fact that the *apparent* width of his K discontinuities from *silver* to lead, is the *same* for each element and is equal to approximately .02A. This defines his slit width, since the writer has shown[12] that for the K limit of the heavier elements, the apparent width of the discontinuity is due entirely to the finite width of slits. One suspects, therefore, that with a rather wide slit, when working near the absorption limit, there may have been a sufficient admixture of scattered radiation from the long wave-length side of the limit to reduce appreciably the observed mass absorption coefficient.

Discussion of Results

There are several points of passing interest, in connection with these results, which it may be not inappropriate to mention in order to call attention to the relative magnitude of the several discontinuities.

Fig. 8 shows to scale, each at the wave-length of its K absorption limit, the relative magnitudes of the K discontinuities for each of the six elements investigated. Here τ_a is the fluorescent atomic absorption coefficient* after making the rather unsatisfactory correction for scattering. It is to be noted that the *absolute* magnitude of the discontinuity increases rapidly with decreasing atomic number. That is, molybdenum, just at

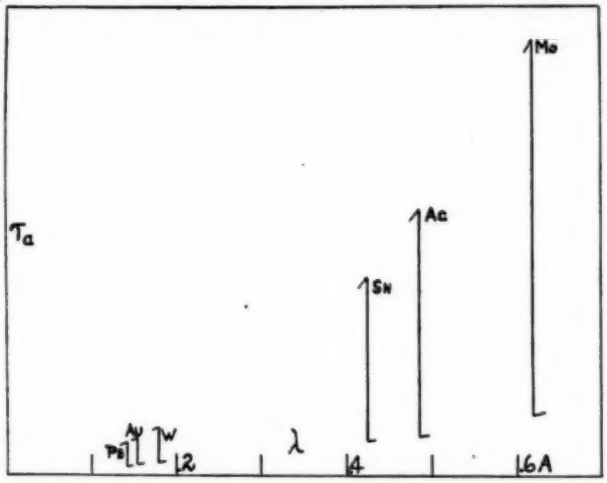

Fig. 8. Showing to scale the relative magnitudes of the K absorption discontinuities for the six elements investigated.

the short wave-length side of its absorption limit is a much better absorber than is lead at the short wave-length side of its limit.

This result is of course to be anticipated from the well known laws of absorption, combined with Moseley's law, which, for the K absorption limit may be written in the form

$$\lambda_K = c'/(N-b)^2$$

where N is the atomic number, and b and c' are constants. If this value of λ_K be introduced into Eq. (1) there results

$$\tau_{max} = c'' N^4/(N-b)^6 \qquad (8)$$

* If the observed values of the mass absorption coefficient μ/ρ be corrected by subtracting the value of the mass scattering coefficient σ/ρ, as determined by the intercept on the μ/ρ axis in Figs. 2-7, one obtains τ/ρ the *fluorescent* mass absorption coefficient. Thus $\mu/\rho = \tau/\rho + \sigma/\rho$. If the values of τ/ρ be divided by the number of atoms per gram in each case, one obtains τ_a, the atomic fluorescent absorption coefficient. And as explained above $\tau_a = \tau_K + \tau_L + \tau_M + \ldots$.

where τ_{max} is the *maximum* value of the atomic absorption coefficient just at the short wave-length side of the K limit, and c'' is another constant, the assumption being made, of course, that Eq. (1) holds rigorously up to the K limit. If b be neglected in comparison with N, it follows that the maximum value of the atomic fluorescent absorption coefficient just at the short wave-length side of the K limit should be proportional to N^{-2}. A convenient check on Eq. (8) is the determination of b. This can be readily done by putting the equation in the form

$$(c''N^4/\tau_{max})^{1/6}=N-b \tag{9}$$

and plotting a graph between $(N^4/\tau_{max})^{1/6}$ and N.* This graph is shown in Fig. 9, from which it is seen that the value of b which best agrees with these data is about 7.5, much larger than the accepted value of b in Moseley's equation. The data are not sufficiently precise to determine whether

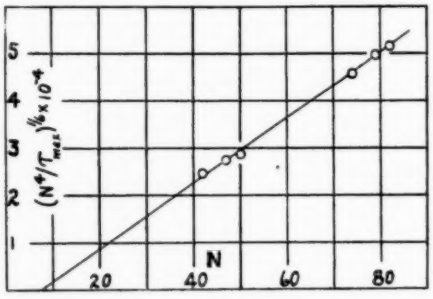

Fig. 9. Graphical determination of b in the term $(N-b)$ of Eq. (8).

this large value of b is due to experimental error, or whether it is due to the fact that Eq. (1), as is well known, is only a close approximation to the true formula.

Comparison with Theory

The experimental values of R_L^K as a function of N are shown by the circles in Fig. 10. The points plotted for molybdenum and silver are the average of those given in Table I. The remaining points are those given in the last column of Table I. While it is obvious that the data do not warrant an attempt to ascertain an empirical relation between R_L^K and N, nevertheless they are sufficient to serve as a check, even though a rough one, on the several theories proposed.

Thomson's theory.[1] This well known theory was proposed by Thomson at least as early as 1903. It is based on the assumption that the electron

* Values of $(N^4/\tau_{max})^{1/6}$ were computed from the data given in columns 1, 4, 5, 6 and 7 of Table II, λ being expressed in angstroms.

is bound to a fixed position in the atom by simple harmonic forces. The displacement of the electron from this equilibrium position is then computed when a pair of rectangular but oppositely directed pulses, each of thickness d, passes over the electron. The potential energy stored up in this displacement is extracted from the pair of pulses and is emitted as fluorescent energy of wave-length λ_0 after the pulse has passed. This leads to the following absorption coefficient per electron, τ_e, *for a single pair of pulses*

$$\tau_e = 4\pi^3 \frac{e^2}{mc^2} \frac{1}{\lambda_0^2} d^3 , \tag{10}$$

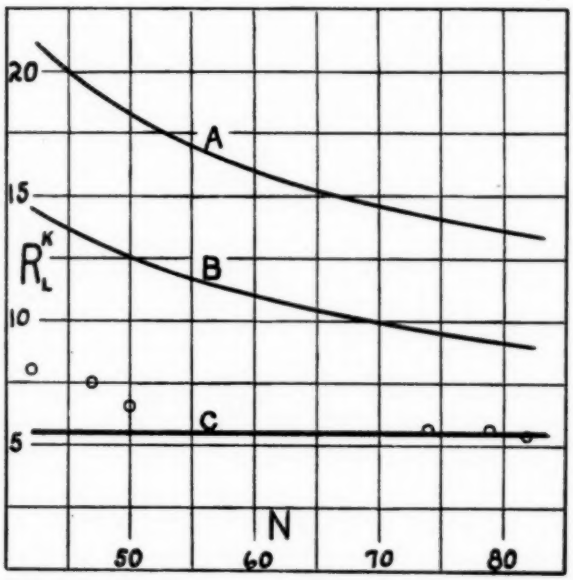

Fig. 10. Variation of the absorption discontinuity with atomic number. Curve A: Kramers' theory as modified by Eq. (26). Curve B: Theories of Thomson (Eq. (13)), of Compton (Eq. (15)), and of de Broglie (Eq. (21)). Curve C: Kramers' original theory (Eq. (24)). The circles represent actual observations.

or if we identify d with $\lambda/2$, where λ is the wave-length of the incident x-rays, we have

$$\tau_e = \frac{\pi^3}{2} \frac{e^2}{mc^2} \frac{1}{\lambda_0^2} \lambda^3 . \tag{11}$$

It is interesting to point out that on Thomson's theory the term d^3, or in more modern terms λ^3, is obtained by the following steps. (1) The electron experiences a uniform acceleration for a time which is proportional to d and is therefore displaced through a distance proportional to d^2. (2) The potential energy stored up against return forces is pro-

portional to d^4; but the incident energy must be proportional to d. (3) The absorption coefficient, which is the ratio of absorbed to incident energy, is therefore proportional to d^3. The atomic absorption coefficient τ_a is obtained by summing up the term $1/\lambda_0^2$ for each electron in the atom, hence

$$\tau_a = \frac{\pi^3}{2}\frac{e^2}{mc^2}\sum\frac{n_0}{\lambda_0^2}\lambda^3 \tag{12}$$

where for the atom under consideration n_0 represents the number of electrons emitting characteristic radiation of wave-length λ_0. Eq. (12) can be put into a form to be compared with more recent formulas by using the relation

$$\frac{1}{\lambda_0^2} = \frac{h^2\nu_0^2}{h^2\,c^2} = \frac{E_0^2}{h^2\,c^2}$$

which gives

$$\tau_a = \frac{\pi^3}{2}\frac{e^2}{mh^2c^4}(n_K E_K^2 + n_L E_L^2 + \cdots)\lambda^3 \tag{13}$$

where, in modern notation, n_K, n_L . . . stand for the number of electrons in the K, L . . . levels respectively and E_K, E_L . . . are the corresponding binding energies. To check this with experiment, (13) gives for Bi in the K region, assuming $n_K = 2$, $n_L = 8$, $n_M = 18$ and averaging the multiple values of E_L and E_M usually found in tables,

$$\tau_a = 5.20 \times 10^6\,\lambda^3$$

whereas (1) gives for B_i

$$\tau_a = 1.06 \times 10^6\,\lambda^3$$

It appears therefore that Thomson's formula gives a value of τ_a about five times too large.

There are reasons why we might expect (13) to give too large values. The discussion is based on the passage of a *single* pair of pulses over the electron. If a *train* of pulses is considered, each succeeding pulse produces an additional displacement and an increased restoring force. The result is that less energy is removed per pulse the greater the displacement. For a large number of pulses it is obvious that the average energy removed per pulse would be less than for the first pulse; i.e. the absorption coefficient for a wave train should be less than for a single pulse.

It is observed* that the introduction into (13) of Moseley's approximate law $\nu \propto N^2$ for the relation between an absorption limit and atomic number leads directly to an equation of the form of (1).

* See also A. H. Compton, Phys. Rev. **14**, 249 (1919).

Compton's theory. This is somewhat similar to Thomson's theory in that it applies the fundamental laws of dynamics to "electrically charged particles capable of executing damped harmonic oscillations." An equation for the absorption coefficient per electron is then derived which involves the damping coefficients of the forced and of the free vibrations and the corresponding frequencies. This equation is simplified by approximation, and the exponent of λ is determined by an empirical evaluation, the resulting expression for the *atomic* absorption coefficient being given by

$$\tau_a = 2\pi \frac{e^2}{mc^4}\left(n_K \frac{1}{\lambda_K^2} + n_L \frac{1}{\lambda_L^2} + \cdots\right)\lambda^3 \tag{14}$$

which, when put in the form

$$\tau_a = 2\pi \frac{e^2}{mh^2c^4}(n_K E_K^2 + n_L E_L^2 + \cdots)\lambda^3 \tag{15}$$

is identical with (13) except for the factor involving π.
For bismuth, this gives

$$\tau_a = 2.10 \times 10^6 \lambda^3$$

a result approximately twice the experimental value. Compton's formula does not give an independent theoretical justification for the λ^3 term.

de Broglie's theory.[2] This theory is based on the assumption that it is possible to set up conditions of equilibrium between atoms and a radiation field such that the rate of absorption of energy by the atoms in the process of the *photo-electric emission of electrons* is just equal to the rate of emission of energy as a result of the converse process, namely the "de-ionizing" of atoms by the free electrons. The equation to express this fact assumes the following form

$$N_{i_p} A_{i_p}^{n} E_p dt = \frac{1}{\eta_p} N_n \int_{\nu_p}^{\infty} h\nu F(\nu)\, \rho(\nu, T) d\nu\, dt \tag{16}$$

where $A_{i_p}^{n}\, dt$ represents the fraction of ionized atoms, N_{i_p} per cc which take up free electrons in time dt and return to the normal state n, from the ionized state i_p, giving out energy E_p per atom; N_n is the number of normal atoms per cc taking part in the equilibrium process; $F(\nu)$ is a function of the frequency which states the fraction of normal atoms which become ionized in unit time, for unit density of the radiation of frequency ν, the energy density being given by Wien's equation

$$\rho(\nu, T) d\nu = (8\pi h/c^3)\nu^3 e^{-h\nu/kT} d\nu. \tag{17}$$

$1/\eta_p$ represents the fractional part of the absorbed energy which is returned in the corresponding fluorescent radiation. If $F(\nu)$ be evaluated and multiplied successively by (1) the number of atoms $N\,dx$ per square centimeter of an absorbing material of thickness dx, (2) the energy *density* of the incident radiation of frequency ν, and (3) the energy $h\nu$ absorbed by each atom in the process of ionization, the result is the rate of absorption of energy. If this result be divided by the rate at which energy is incident on the square centimeter we have the absorption coefficient which is found to be

$$\tau_a=(1/8\pi ckT)\lambda^3\sum A_{i_p}^{n}\,E_p\eta_p\,. \tag{18}$$

The summation is to be extended to all the electrons of the atom. It is assumed that

$$\eta_p A_{i_p}^{n}=KE_pT \tag{19}$$

K is evaluated and found to be

$$K=\frac{8\pi^2}{c^3}\,\frac{k}{h^2}\,\frac{e^2}{m} \tag{20}$$

If (19) and (20) be put in (16) and the result extended to all the electrons of the atom we have

$$\tau_a=\pi(e^2/mh^2c^4)(n_{\mathrm{K}}E_{\mathrm{K}}{}^2+n_{\mathrm{L}}E_{\mathrm{L}}{}^2\cdot\ \cdot\ \cdot\ \cdot\ )\,\lambda^3 \tag{21}$$

a result identical with Thomson's value, Eq. (13), except for the factor involving π. For bismuth Eq. (21) gives, for $\lambda<\lambda_{\mathrm{K}}$,

$$\tau_a=1.14\times10^6\lambda^3$$

in excellent agreement with experiment. It is to be observed that the λ^3 term appears in (18) because of the introduction of Wien's Eq. (17) in which appears the term ν^3.

Kramers' Theory. This has several points in common with deBroglie's theory. Both assume Wien's law of energy distribution and the possibility of thermodynamic equilibrium. Kramers then starts with the assumption that

$$NP_nQ_{n\to i}=NP_iQ_{i\to n} \tag{22}$$

where P_n represents the fraction of a total number N of atoms which are in an n or normal state and $Q_{n\to i}$ represents the fraction of these per second which pass from the normal to the ionized state i. Similarly P_i represents the fraction of N atoms which are in the ionized state, a fraction $Q_{i\to n}$ of which return per second to the n state. P_n and P_i are con-

nected by Boltzman's probability principle. $Q_{n\to i}$ involves the spectral energy density of the exciting radiation (given by Wien's law) and the atomic absorption coefficient, τ_a' which, since τ_a' has the dimensions of an area, may be regarded as "the effective cross-section" of an atom for intercepting radiation. $Q_{i\to n}$ on the contrary involves the inverse process, namely the effective cross section τ_β of an ionized atom for intercepting electrons. A simple relation is thus established between τ_a' and τ_β. By aid of the correspondence principle and the classical laws of radiation of an electron describing an orbit *past a positively charged nucleus Ne*, the value of τ_β is determined. The final value of τ_a' may be put in the form

$$\tau_a' = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10}m}{c^4 h^6} g' \frac{1}{k^4(k+1)} N^4\lambda^3 \tag{23}$$

where τ_a' refers to the absorption coefficient of a nucleus *Ne*, with a *single* electron in the k quantum orbit, and g' is a constant "which does not differ much from unity." If it be assumed that we can compute the *atomic* absorption coefficient τ_a by summing up (23) for all the electrons of a neutral atom of atomic number N we have

$$\tau_a = \frac{64\pi^4}{3\sqrt{3}} \frac{e^{10}m}{c^4 h^6} g' \left(\frac{2}{1.2} + \frac{8}{2^4\ 3} + \frac{18}{3^4\ 4}\right) N^4\lambda^3 \tag{24}$$

where 2, 8, 18 . . . . represent the respective number of electrons in quantum rings 1, 2, 3. . . . .

Computing, as before, the absorption coefficient for bismuth we have (assuming $g'=1$),

$$\tau_a = 60\times 10^4\lambda^3 ,$$

a value which is about half the experimental value.

Although difficult to trace, it appears that the term λ^3 appears in Kramers' formula on account of the introduction of Wien's law, and the term N^4 apparently comes from the application of classical electrodynamics to the radiation of an electron as it passes a nucleus of charge *Ne*.

As Kramers points out, Eq. (23) is derived for the case of a nucleus of charge *Ne* and a single electron. It can therefore be expected to be only an approximation when applied to all the electrons of an atom. The approximation may be expected to be of the same order as is found in the case of Bohr's theory of the hydrogen spectrum when applied to elements of higher atomic number. Indeed, by use of Bohr's equation for the energy of a given quantum orbit k, namely

$$E_k = h\nu_k = (2\pi^2 mN^2e^4/h^2)\ (1/k^2)$$

we can re-write (23) as follows

$$\tau_a' = \frac{16}{3\sqrt{3}} g' \frac{e^4}{mh^2c^4} \frac{E_k^2}{k+1} \lambda^3 \tag{25}$$

It seems reasonable to extend Eq. (24) so as to include all the electrons of a neutral atom by writing

$$\tau_a = \frac{16}{3\sqrt{3}} g' \frac{e^4}{mh^2c^4} \left(\frac{n_K E_K^2}{1+1} + \frac{n_L E_L^2}{2+1} \cdots \right) \lambda^3 \tag{26}$$

If now, in using (26) we put in the *experimental* values of E_K, E_L . . . the formula should be freed of the limitation of a *single* electron around a nucleus *Ne* and should apply generally. Computing τ_a for bismuth in this way gives

$$\tau_a = 50 \times 10^4 \lambda^3 .$$

It is to be observed that (13), (15) and (21) are identical, except for the value of the factor involving π. However (26) differs from these three not only in the corresponding numerical factor, but in dividing each of the terms E^2 in the bracket by $(k+1)$. *It is in reality this factor* $(k+1)$ *which reduces the value of* τ_a *computed from* (26) *to about half the correct value.* If this factor be omitted the value of τ_a given by (22) is *correct within experimental error for* $\lambda < \lambda_K$.

We are now in position to compare these several theories as regards their prediction of the magnitude of the K absorption discontinuity as expressed by the value of R_L^K. It is evident that Eqs. (13), (15), and (21) give identical values of R_L^K namely:

$$R_L^K = \frac{n_K E_K^2 + n_L E_L^2 + n_M E_M^2 + \cdots}{n_L E_L^2 + n_M E_M^2 + \cdots} \tag{27}$$

while for (24) R_L^K is independent of N and is given by

$$R_L^K = \frac{1 + 1/6 + 1/18 + \cdots}{1/6 + 1/18 + \cdots} = 5.5 \tag{28}$$

For (26) we have, on the contrary,

$$R_K^L = \frac{\frac{n_K}{2} E_K^2 + \frac{n_L}{3} E_L^2 + \frac{n_M}{4} E_M^2 \cdots}{\frac{n_L}{3} E_L^2 + \frac{n_M}{4} E_M^2 \cdots} \tag{29}$$

In evaluating (27), (28) and (29) it is assumed that it is unnecessary to include limits beyond the M limits, and that the values of n_K, n_L and n_M

are respectively 2, 8 and 18. The values of E_K, E_L and E_M used are those obtained partly from Sommerfield's "Atomic Structure and Spectral Lines," and partly from Robinson (Proc. Roy. Soc. **104,** 455 (Nov. 1923). There has been no attempt to weight the multiple values of E_L and E_M; the average values of E_L^2 and E_M^2 have been used. The data are shown in Table III. The values of R_L^K given by the two equations are shown graphically in Fig. 10, curve A corresponding to Eq. (29) (Kramers' theory

TABLE III

Element		E_K	E_L*	E_M*	R_L^K Eq. (27)	R_L^K Eq. (29)
Pb	82	6463	1080	233	9.1	13.4
Au	79	5940	985	207	9.2	13.5
W	74	5114	833	170	9.6	14.2
Sn	50	2148	311	50	12.4	18.2
Ag	47	1879	263	36	13.3	19.7
Mo	42	1473	197	27	14.4	21.3

* "Root-mean-square" values.

Values of E are given in terms of ν/R, where ν is wave-number and R is the Rydberg constant.

as modified in Eq. (26)), and curve B to Eq. (27). The line C in Fig. 10 gives the ratio predicted by Kramers' original Eq. (24). It is seen that the observed values correspond most closely to Kramers' Eq. (24), but this agreement must be regarded as fortuitous, since there can be no doubt that a multiple charged nucleus with a *single* electron behaves quite unlike such a nucleus with its normal quota of electrons. The step from Eq. (23) to (24) cannot therefore be made without some modification. The suggested modification (26) however, gives values of R_L^K (curve A) entirely too large.

While these equations, therefore, do not give values of R_L^K which check closely with experiment, it is very significant that they predict in a qualitative way the variation of R_L^K with N. The experimental data themselves are by no means satisfactory, although probably correct to ten or twenty percent.

It is hoped to improve the precision with which these measurements can be made, and to obtain values of R_L^K for a larger number of elements.

CORNELL UNIVERSITY,
September 11, 1925.

MEASUREMENT OF THE REFRACTION OF X-RAYS IN A PRISM BY MEANS OF THE DOUBLE X-RAY SPECTROMETER

By Bergen Davis and C. M. Slack

Abstract

In the double spectrometer used, x-radiation was reflected from a crystal surface A through a slit S on to a second crystal surface B, and thence to the ionization chamber. Surfaces A and B were obtained by splitting a single crystal of calcite. The curve obtained for Mo Kα by rocking B is a triangle with base about 8 seconds wide. The effect of interposing a *prism of aluminum* (angle 166°) between S and B was to shift the curve 5.62″ on the average, giving $1-\mu=1.68\times10^{-6}$. The value calculated from the Lorentz dispersion formula is 1.77×10^{-6}. For Cu Kα the shift was 5.53″ for a 116° prism, giving $1-\mu=8.4\times10^{-6}$ as compared with the calculated value 8.36×10^{-6}. The accuracy of this method is thus within 5 percent.

EVIDENCE of the direct refraction of x-rays on passing through a prism was long sought for without success. The effect is so minute that its direct detection is difficult.

Recently, however, the direct bending in a prism has been measured by the photographic spectrometer method in the laboratory of Professor Siegbahn.[1] Shortly afterward the direct refraction in a prism was measured by the authors,[2] using the single ionization spectrometer. A serious defect of the single ionization spectrometer for this purpose arises from the fact that the maxima of the energy curves are shifted not only by refraction but by the unsymmetrical absorption of the beam in the prism.

Refraction at the surface of a crystal in the case of crystal reflection had already been quite accurately measured by Bergen Davis and R. von Nardroff[3] and by C. C. Hatley,[4] using the ionization spectrometer.

The present paper describes the application of the *double x-ray spectrometer* to the measurement of refraction in a prism. This method is capable of considerable accuracy. A bending of the beam of x-rays as small as one-tenth second of arc can be observed when conditions are favorable.

[1] Larsen, Siegbahn and Waller, Proc. Am. Phys. Soc., Phys. Rev. **25,** 235 (Feb. 1925)

[2] Bergen Davis and C. M. Slack, Proc. Am. Phys. Soc., Phys. Rev. **25,** 881 (June 1925).

[3] Bergen Davis and R. von Nardroff, Proc. Nat. Acad. Sc., **10,** (Feb. 1924) also (Sept. 1924).

[4] C. C. Hatley, Phys. Rev. **24,** 486 (Nov. 1924).

The method will be at once clear by reference to Fig. 1. *A* and *B* are two crystals of split Iceland-spar (calcite). The two reflecting surfaces are the divided halves of the same crystal. The surface of *B* on which the rays fall is the surface that coincided with the reflecting surface of *A* before cleavage. Care was taken to mount the crystals without abrading the reflecting surfaces in any way. The percent reflection and still more important, the narrowness of the "rocking" curves, depends on the virgin condition of these surfaces.[5]

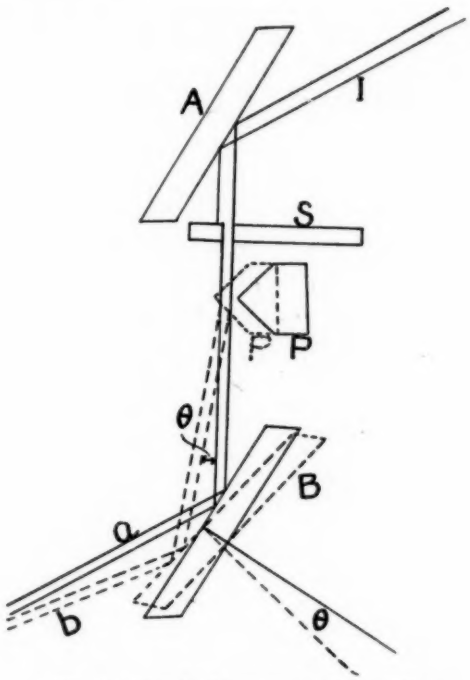

Fig. 1. The double x-ray spectrometer.

The narrow beam *I* of incident x-rays is reflected from crystal *A* through a limiting slit *S* to crystal *B*, and from *B* to the ionization chamber. Crystal *B* is mounted in such a way that it can be turned through a small measured angle as desired. This is accomplished by means of a long arm attached to the crystal table which is operated by a tangent screw. The hand wheel that turns the tangent screw is so divided that one scale division on the edge of wheel represents one-half second of arc of rotation of crystal. The details of this arrangement have been previously described (see Fig. 2 of Davis and Stempel[5]).

[5] Davis and Stempel, Phys. Rev. **17**, 608 (May 1921).

The beam of homogeneous x-rays after passing through slit S falls on crystal B and is reflected into the ionization chamber. This beam is marked a in Fig. 1. Maximum reflection is obtained when the reflecting planes of B are parallel to those of A. If now crystal B be turned (rocked) a small measured angle each side of this maximum position, energy distribution curves are obtained (curve a, Fig. 2). By careful adjustment of

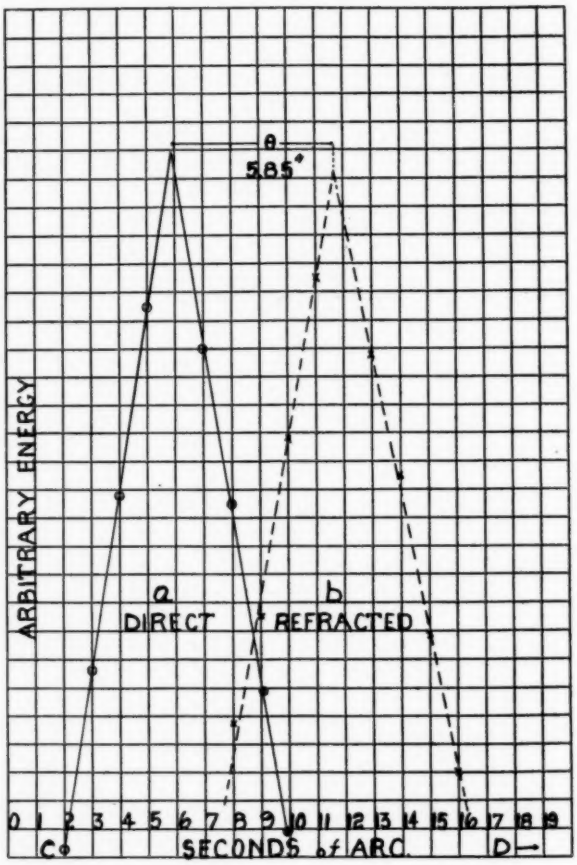

Fig. 2. Specimen curves showing the refraction in an aluminum prism.

the crystals these rocking curves could be made quite narrow. The width at half-maximum was less than 6″ of arc in the case of Mo Kα radiation. The position of the maximum of the curves could be determined to about one-tenth second of arc.

The prism P in which refraction is to be measured is mounted on a carriage with a fine screw so that it may be run in and out of the path of the x-ray beam as desired. When the prism is in the path of the beam,

the ray is refracted through an angle θ as shown. Crystal B is now rotated to reflect this refracted beam. A new rocking curve is obtained. The angular distance of the peak of this curve is equal to θ, the angle of refraction. The great advantage of the double x-ray spectrometer over the single is that the unequal absorption of the rays in the prism does not affect the position of the peak of the curves at all. This was directly tested by experiment. A piece of lead with a flat edge (not a prism) was mounted in place of the prism. When this piece of lead was pushed partially across the beam, the rocking curve was diminished in intensity, but the position of the peak was not altered.

Specimen curves for refraction in an aluminum prism are given in Fig. 2. Curve a was obtained with the direct beam a (Fig. 1) and curve b with the refracted beam b. Measurements were made for two frequencies, Mo Kα (λ.7078) and Cu Kα (λ1.537). The refracting angle R of the prism was 166° in case of λ.7078 and was 116° in case of λ1.537.

When the prism is symmetrically placed (position of minimum deviation) the index of refraction μ may be expressed by

$$\mu = 1 - \delta \; ; \; \delta = -\theta/2 \tan \tfrac{1}{2}R$$

The sign of θ is negative for bending in the direction indicated in the figure.

The results obtained are given in the table.

λ	R	θ (obs)	Mean θ	$\delta \times 10^{-6}$ (obs)	$\delta \times 10^{-6}$ (calc)
.7078	166°	5.85″ 5.46 5.75 5.50 5.55	5.62″	1.68	1.77
1.537	116°	5.40 5.60 5.60	5.53″	8.4	8.36

The last column of the table gives the values of δ computed from the Lorentz dispersion formula. In the case of the radiation here used, the frequency is so far removed from the natural resonance frequencies of the aluminum atom that the simplified form

$$\delta = \frac{e^2}{2\pi m} \frac{1}{V^2},$$

was used for the computations.

The accuracy obtained in these measurements is well within ± 5 percent. This accuracy might be increased by repeated measurements and in particular by maintaining constant temperature.

It was found that the position of the peaks of the curves often shifted during the course of a run. It was observed that the temperature also changed at the same time. On those occasions when the temperature was practically constant the shift was quite small. This shift apparently arises from an unequal expansion or contraction of the various parts of the apparatus, particularly the parts of the mechanism operating crystal B. Another source of error was the measurement of the angle R of the prism and the placing of it in a symmetrical position.

PHOENIX PHYSICAL LABORATORY,
COLUMBIA UNIVERSITY,
October 20, 1925.

THE ABSORPTION SPECTRA OF THE VAPORS OF ALUMINUM, GALLIUM, INDIUM AND THALLIUM IN THE ULTRAVIOLET

By John G. Frayne and Alpheus W. Smith

Abstract

(1) *Absorption in heated vapors.* The metals were vaporized in a graphite tube 15 cm long heated with an oxyacetylene torch to temperatures up to 2000°C. A tungsten under-water condensed spark provided a continuous spectrum. *Aluminum.* At about 1200°C the first 7 pairs of the first subordinate series were absorbed. The relative intensities differ from what might be expected from the Bohr theory standpoint. No absorption was observed for the second subordinate series. *Gallium.* At a temperature of about 1500°C, 17 prominent lines appeared, including the first 4 pairs of the first and second subordinate series and the 5th term of the $2p_1-ms$ series. *Indium.* At a temperature of about 1200°C, 18 lines appeared, including the first 3 pairs of the first subordinate series, the first 5 pairs of the second subordinate series and the 4th term of the $2p_1-md$ series. *Thallium.* At 400°C, 4 lines of the $2p_2-ms$ and 4 of the $2p_2-md$ series appeared, widening into bands with increasing temperature. At 800°C, lines from the $2p_1$ level appeared as fine absorption lines. These results verify those of Grotrian. (2) *Absorption in the arc.* A bead of the metal was placed in a crater. *Aluminum.* In a 15 amp. arc the lines of the $2p_2-md$ and $2p_1-md$ ($m=5$ to 11) were completely absorbed. *Indium.* Besides the resonance lines $2p_2-2s$ and $2p_2-3d$, the lines $2p_1-2s$ and $2p_2-3d$ were completely absorbed. (3) *Relative behavior of lines from $2p_1$ and $2p_2$ levels.* The lines for the $2p_1$ level for gallium and indium are as readily absorbed as those for the $2p_2$ level and therefore may also be resonance lines.

Introduction

INVESTIGATION of the absorption spectra of aluminum and thallium vapors has been made by McLennan, Young and Ireton.[1] Using the method of arc reversals they found band absorption corresponding to some of the higher members of the $2p_2-ms$ and $2p_2-md$ series. Their results will be discussed below. Grotrian[2] found the first pair of the first and second subordinate series in gallium vapor completely absorbed. In a previous paper[3] he tells of having found several members of the first and second subordinate series absorbed in the vapors of indium and thallium. He used the method of passing a continuous ultraviolet spectrum through the vapor of the metal in an evacuated quartz tube. He

[1] McLennan, Young and Ireton, Roy. Soc. Can. Proc., **13**, 9 (1919).
[2] Grotrian, Zeits. f. Physik **18**, 169 (1923).
[3] Grotrian, Zeits. f. Physik **12**, 218 (1922).

was limited to temperatures of 1200°C and found few lines below 2400A. In a recent paper Narayan, Gunnayya and Rao[4] found band and line absorption in thallium vapor corresponding to several arc lines, including 3776A ($2p_2-2s$). Guthrie[5] and later Wood and Guthrie[6] made investigations of absorption in thallium vapor. Uhler and Tanch[7] found the lines 4511A ($2p_1-2s$) and 4101A ($2p_2-2s$) absorbed in indium vapor.

The present investigation was undertaken with a view to extending Grotrian's work to aluminum. Further, since the method described below made it possible to use temperatures as high as 2000°C, it was thought that new information could be obtained for the vapors of gallium, indium and thallium. It was also thought that further study of absorption in this group might help put a more satisfactory construction on the real meaning of the $2p_1$ level. At the present time it is considered a metastable level, while the $2p_2$ level is chosen as the stable orbit. There is very little experimental evidence for such a distinction, as direct resonance measurements have only been reported on thallium. It is a well known fact that resonance lines are readily absorbed in the normal vapor of the element, but the elements of this group not only have their resonance lines but also lines from the $2p_1$ level appear as absorption lines. The difference $2p_2-2p_1$ is small for aluminum, about .10 volt, increasing to about .96 volt in thallium. It is true that Mohler and Ruark[8] found a resonance potential of .9 volt in thallium vapor and Jarvis[9] has found a similar potential of .3 volt in gallium vapor. Grotrian found that absorption of lines from the $2p_2$ level took place at a lower temperature than from the $2p_1$ level, the temperature difference increasing from about 100°C in gallium to about 400°C in thallium. However, the fact that he did find lines from the $2p_1$ level strongly absorbed, seemed to indicate that they might be placed in the same category as those from the $2p_2$ level.

Experimental Procedure

The metal under investigation was placed in a graphite tube 15 cm long open at both ends. An oxyacetylene torch was used as the source of heat. This method has been already described by Zumstein[10] who used it in a study of the absorption spectra of copper, silver and gold. In the

[4] Narayan, Gunnayya and Rao, Roy. Soc. Proc. **106,** 596 (1924).
[5] Guthrie, Dissertation (1908).
[6] Wood and Guthrie, Astrophys. J. **29,** 211 (1909).
[7] Uhler and Tanch, Astrophys. J. **55,** 291 (1922).
[8] Mohler and Ruark, J.O.S.A. **7,** 819 (1923).
[9] Paper not yet published.
[10] Zumstein, Phys. Rev. **25,** 523 (1925).

case of aluminum and thallium it was found necessary to pass a stream of nitrogen over the metal to prevent oxidation. At very high temperatures the aluminum combined with the nitrogen, making it difficult to secure sufficiently dense vapor to show absorption.

The continuous ultraviolet spectrum was produced by a condensed spark between tungsten electrodes under water. The spark circuit was similar to that described by Hulburt[11] with the exception that the auxiliary gap was an ordinary air gap with an air blast between the electrodes. This proved to be a very satisfactory arrangement, giving a continuous spectrum between 8000A and 2000A. A Féry type spectrograph was used throughout the work.

On account of the rapidity with which the graphite tube heated it was found impossible to take observations at temperatures which differed by less than 50°C.

Experimental Results

Aluminum. Several absorption lines appeared about 1200°C. They were found to correspond to well defined arc lines (see Table I). The first six pairs of the first subordinate series were absorbed, the absorption being more prominent in the shorter wave-lengths. The line 3092A ($2p_1-3d$) was more strongly absorbed than 3082A ($2p_2-3d$). Neither the lines 3962A ($2p_1-2s$) and 3944A ($2p_2-2s$) nor any other lines of the second subordinate series were absorbed.

Table I

Absorption spectrum of aluminum vapor

$\nu=2p_2-md$		*$\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
3	3082.16	3	3092.84
4	2567.997	4	2575.411
5	2367.064	5	2373.360
6	2263.453	6	2269.212
7	2204.627	7	2210.046
8	2168.805	8	2174.028
9	2145.390	9	2150.59
†10	2129.44	†10	2134.70
†11	2118.52	†11	2123.38

* New absorption lines.
† Absorbed in the arc.

The arc reversal method also was used to detect absorption. A small bead of the metal was placed in the crater of the positive carbon and vaporised in a 10 ampere arc. Some of the spectrograms showed complete

[11] Hulburt, Phys. Rev. **24**, 129 (1924).

absorption of five pairs of the first subordinate series, beginning with the fourth pair. In addition, narrow reversals were observed in the second and third pair as well as in the first pair of the second subordinate series. When a 15 ampere arc was used absorption was extended to the third pair of the first subordinate series.

Gallium. One gram of gallium gave sufficient vapor for absorption when heated to a temperature of about 1500°C. The first four lines of

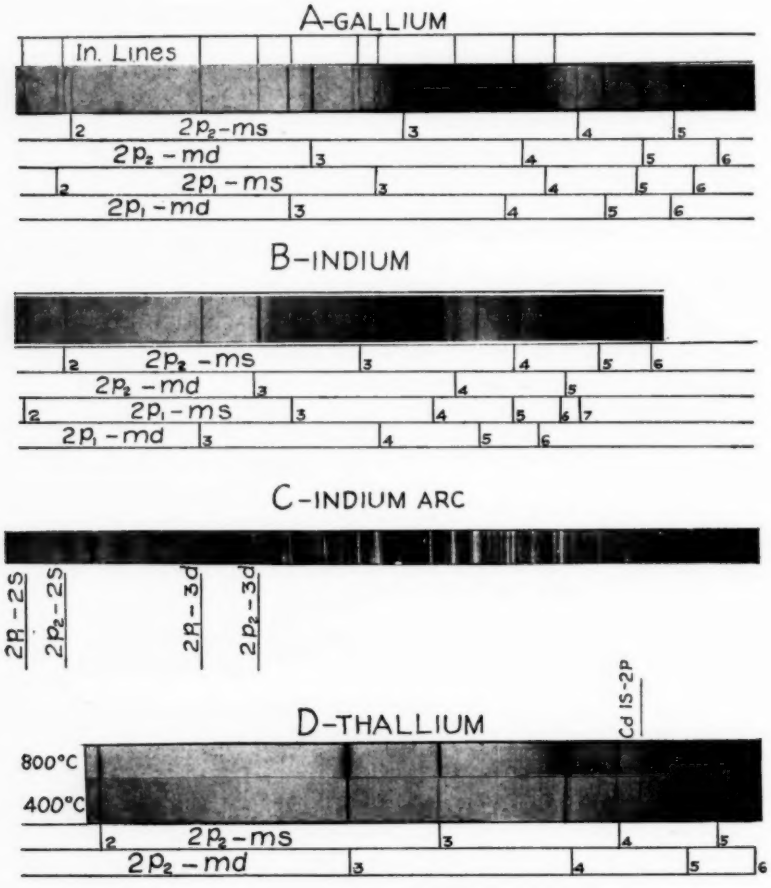
A-GALLIUM
In. Lines
2 2p2-ms 3 4 5
2p2 - md 3 4 5 6
2 2p1 - ms 3 4 5 6
2p1 - md 3 4 5 6
B-INDIUM
2 2p2 - ms 3 4 5 6
2p2 - md 3 4 5
2 2p1 - ms 3 4 5 6 7
2p1 - md 3 4 5 6
C-INDIUM ARC
2p1 - 2s
2p2 - 2s
2p1 - 3d
2p2 - 3d
D-THALLIUM
Cd 1S-2P
800°C
400°C
2 2p2 - ms 3 4 5
2p2 - md 3 4 5 6

Plate I

the $2p_2 - ms$ and $2p_2 - md$ series were strongly absorbed. In addition, the first five lines of the $2p_1 - ms$ and $2p_1 - md$ series were absorbed. Band absorption occurred between 2620 and 2480A. This band became more pronounced at higher temperatures. The wave-lengths of the gallium lines given in Table II are taken from the Astrophysical Journal[8]

of May, 1922. Plate IA is a reproduction of one of the spectrograms taken with this vapor.

In addition to the gallium lines there appeared as impurities the indium lines $2p_2-ms$ ($m=2$ to 4), $2p_2-md$, ($m=3$ to 5), $2p_1-ms$ ($m=2$ and 3) and $2p_1-md$ ($m=2$ and 3).

TABLE II

Absorption spectrum of gallium vapor

$\nu=2p_2-ms$		$\nu=2p_2-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4032.975	3	2874.24
*3	2659.873	*4	2450.078
*4	2371.325	*5	2294.202
*5	2255.034	*6	2218.039
$\nu=2p_1-ms$		$\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4172.06	3	2944.175
*3	2719.66	*4	2500.714
*4	2418.699	*5	2338.596
*5	2297.869	*6	2259.227
*6	2236.103		

* New absorption lines.

Indium. The lines absorbed in indium vapor are given in Table III. The first three lines of the $2p_2-ms$ and the first four of the $2p_2-md$ series

TABLE III

Absorption spectrum of indium vapor

$\nu=2p_2-ms$		$\nu=2p_2-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4101.764	3	3039.356
3	2753.889	4	2560.157
4	2460.079	5	2389.543
5	2340.191	12?	2181.70
*6	2278.20		
$\nu=2p_1-ms$		$\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	4511.38	3	3258.565
3	2932.633	4	2713.932
4	2601.756	5	2522.854
5	2468.12	6	2430.70
6	2399.25		

* New absorption lines.

were strongly absorbed. In addition the first five members of the $2p_1-ms$ and $2p_1-md$ series were absorbed. A line corresponding to the emission line 2181A was absorbed. This may be $2p_2-12s$ but as this leaves the

members of the series from $m=6$ to $m=11$ missing, the line is probably due to an impurity. All of the absorption lines occurred on every picture. Plate IB is a reproduction of a spectrogram taken at a temperature of about 1200°C. The emission spectrum of indium is reproduced in Plate IC. It will be noted that the lines $2p_2-2s$, $2p_1-2s$, $2p_2-3d$ and $2p_1-3d$ were completely absorbed in the arc. Aluminum emission lines were prominent in the arc but none appeared to be absorbed.

Thallium. Grotrian's observation that there was a 400°C difference between the appearance of lines from the $2p_1$ and $2p_2$ levels was verified in this investigation. The lines of the series $2p_2-ms$ ($m=2$ to 5) and $2p_2-md$ ($m=3$ to 6) appeared as fine absorption lines about 400°C. As the temperature increased these lines widened into bands extending asymmetrically toward the red. At 1200°C the lines $2p_2-2s$ and $2p_2-3d$ widened into bands of approximately 50A, while 2379A ($2p_2-4d$) extended about 38A. This latter line was the only one observed by Wood and Guthrie.[6]

TABLE IV

Absorption spectrum of thallium vapor

$\nu=2p_2-ms$		$\nu=2p_2-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	3775.72	3	2767.87
3	2580.14	4	2379.58
4	2315.93	5	2237.84
5	2207.06	*6	2168.61
$\nu=2p_1-ms$		$\nu=2p_1-md$	
m	λ(in I.A.)	m	λ(in I.A.)
2	5350.46	3	3529.43 3519.24
3	3229.75	4	2921.52 2918.32
4	2826.16	5	2710.67
5	2665.57	6	2609.77
6	2585.59	7	2552.53
7	2538.18	8	2517.41
8	2507.94	9	2493.91
9	2487.48	10	2477.49
10	2472.57	11	2465.46
11	2461.93	12	2456.45
		13	2449.49
		14	2443.92
		15	2439.50
		16	2435.80
		17	2433.0

* New absorption lines.

At about 800°C the lines of the series $2p_1-ms$ and $2p_1-md$ appeared as fine absorption lines. These lines did not widen into bands as the tem-

perature was raised. The complete list of lines absorbed in this vapor is given in Table IV. Plate ID shows the lines from the $2p_2$ level only.

Discussion

The appearance of the aluminum lines is not what one would expect from the Bohr theory standpoint. In the first place, the resonance line 3944A ($2p_2-2s$) failed to appear as an absorption line. Secondly, the resonance line 3082A ($2p_2-3d$) appears only as a very faint absorption line, while the line 3092A ($2p_1-3d$) was much more prominent. Finally, the higher members of the series showed stronger absorption than those of longer wave-length. This latter point was also noted by McLennan, Young and Ireton,[1] who studied the absorption spectra by the arc reversal method. They found band absorption corresponding to lines of the $2p_2-ms$ ($m=4.5$ to 8.5) and $2p_2-md$ ($m=6$ to 14) series. They found no absorption of any lines from the $2p_1$ level.

The work of Grotrian[2] with gallium vapor was verified and thirteen new absorption lines discovered. He had found only the lines $2p_2-2s$, $2p_1-2s$, $2p_2-3d$, and $2p_1-3d$. The results of this investigation showed that lines from the $2p_1$ level were just as readily absorbed as those from the $2p_2$ level and that the term *resonance* might be equally applied to any line.

All of the lines found absorbed in indium vapor by Grotrian[3] were obtained on the spectrograms. In addition, the fifth member of the series $2p_2-ms$ (2278A) was strongly absorbed. The complete absorption of $2p_2-2s$, $2p_2-3d$, $2p_1-2s$ and $2p_1-3d$ points strongly to the suggestion that the latter pair might be considered in the same category as the former, which are recognised resonance lines. It is of interest to note that Uhler and Tanch[7] observed only 4511A ($2p_1-2s$) and 4101A ($2p_2-2s$) absorbed in indium vapor.

The results obtained in thallium vapor clearly differentiate between the $2p_2$ and $2p_1$ levels in this atom. The lines of the $2p_2-ms$ and $2p_2-md$ series appear without any of the lines of the $2p_1-ms$ or $2p_1-md$ series. Further, the lines from the $2p_2$ level are radically different from those from the $2p_1$ level in that they widen out into bands with increasing temperature whereas the latter lines remain as fine absorption lines. Only one new line 2168A ($2p_2-6d$) was found in this investigation. McLennan, Young and Ireton[1] found absorption bands in thallium vapor, corresponding to the lines $2p_2-md$ ($m=6$ to 10) and $2p_2-ms$ ($m=5.5$ to 11.5). They failed to find any absorption of lines from the $2p_1$ level. They explained their failure to find 3776A ($2p_2-2s$) by suggesting that the presence of Hg vapor was necessary to cause absorption

of this line. This investigation shows that temperature and density are the controlling factors in the production of lines in the absorption spectrum.

ANTIOCH COLLEGE,
YELLOW SPRINGS, O. (J.G.F.)

MENDENHALL LABORATORY OF PHYSICS,
OHIO STATE UNIVERSITY,
COLUMBUS, O. (A.W.S.)
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POLARIZATION OF RADIATION EXCITED BY ELECTRON IMPACT[1]

By A. Ellett,[2] Paul D. Foote and F. L. Mohler

Abstract

Polarized radiation following electron impact.—If a unidirectional beam of electrons, of velocity slightly in excess of the resonance potential, is projected through a vapor at a very low pressure so that effects due to atomic collision and resonance radiation are negligible, and in the absence of an applied field and resulting Larmor precession, there is reason to suspect that the radiation emitted perpendicular to the electron beam should be partially polarized, especially for lines corresponding to $\Delta j=1$.

Polarization in mercury and sodium vapor.—Experiment showed a polarization of about 30 percent for λ2537 with the greatest intensity of the electrical vibration having a direction perpendicular to the electron beam. No polarization was detected for the unresolved sodium D-lines, confirming the recent observation of Kossel and Gerthsen.

Polarization in mercury with field of 3 gauss.—A field parallel to the electron beam produced no effect. With the field perpendicular to the beam the radiation along the field was unpolarized while that perpendicular to the field was reduced in polarization to 13 percent. These results suggest that the atom radiates with the same distribution of polarization and intensity as in zero field but with the atom rotated through an angle determined by the time of excitation and the precessional velocity.

IN the complete absence of an electric or magnetic field, the atoms of a gas at very low pressure are oriented at random. Let j_0 represent the number of units $(h/2\pi)$ of angular momentum characterizing each atom in the normal state. The effect of an inelastic impact with an electron is the production of an atom in an excited state having an increased amount of energy and an angular momentum j. In collisions at a velocity only slightly greater than that corresponding to the resonance potential, the final velocity of the electron is practically zero. Under these conditions it would appear that the vector representing the angular momentum transferred to the atom should be directed perpendicularly to the velocity of the electron before the collision.

Let us consider the case when the atom absorbs one unit of angular momentum $(j=j_0+1)$ which is subsequently radiated as a quantum of circularly polarized light. The axis of the circular vibration coincides in direction with j. For a uniform distribution of the j_0 vectors the statistical

[1] Published by permission of the Director of the National Bureau of Standards of the U. S. Department of Commerce.

[2] National Research Fellow.

distribution of the j vectors, following collision with a unidirectional, univelocity beam of electrons, is readily obtained from simple geometrical relations. The j axis of any atom should remain fixed in direction since the assumption of no external field precludes precession during the time of excitation. The circular vibration emitted, as viewed by an observer looking perpendicularly to the electron beam, appears in general elliptically polarized. The elliptical vibration may be resolved along the directions parallel and perpendicular to the beam and the sums $I_{\parallel}$ and $I_{\perp}$ of the corresponding intensities for the circularly polarized radiations from all of the atoms representing the various orientations of j, may be calculated. The following formula for the resulting polarization of the radiation is obtained in the above described manner.

$$\text{Polarization} = P = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + I_{\perp}} = \frac{3(1 - j_0^2/j^2)}{9 - j_0^2/j^2}. \tag{1}$$

The experiment therefore appeared to afford a direct means for differentiating between the three systems of inner quantum numbers proposed by Sommerfeld, Landé and Bohr. Thus for the λ2537 line of mercury, as shown in Table I, the assumption of 0, 1/2 and 1 unit of angular momentum for the normal state of the mercury atom leads to values of the polarization which are readily distinguishable experimentally. Unfortunately these considerations fail entirely to explain the results obtained.

TABLE I

Percent of polarization computed from Eq. (1)

j_0	j	$I_{\parallel}/I_{\perp}$	P
0	1	2.00	33.3%
1/2	3/2	1.86	30
1	2	1.69	25.7
3/2	5/2	1.57	22.2

The experiment has been carried out with the λ2537 line of mercury and the sodium D-lines. Several different forms of discharge tube were employed, one found quite satisfactory for mercury being shown in Fig. 1. The hot wire source was a narrow platinum ribbon with a small spot of calcium-barium mixture directly opposite the pair of diaphragms of 3 mm opening. On making the focusing cylinder slightly positive relative to the activated spot on the platinum, a well defined beam of electrons could be projected into the observation chamber. By means of a quartz-glass re-entrant graded seal with a plane quartz window fused in the end, the scattering effect of the vapor surrounding the beam was reduced to a minimum. The chamber through which the beam passed was a platinum

cylinder cut away in front for the observation window and in back so that the line of sight passed into the horn on the left. The entire tube was painted on the outside with lamp black, so that the horn made a very effective light trap for scattered radiation from the filament. The mercury vapor was at a pressure corresponding to $-18°C$, the lower part of the tube being immersed in an ice-salt bath. The vapor pressure on the mercury pump side was reduced by a liquid air trap. At this low mercury pressure the effect of secondary resonance radiation is practically negligible. For example, a beam of $\lambda 2537$ radiation projected through a bulb of mercury vapor at $-18°C$ is sharply defined, whereas at $0°C$ the

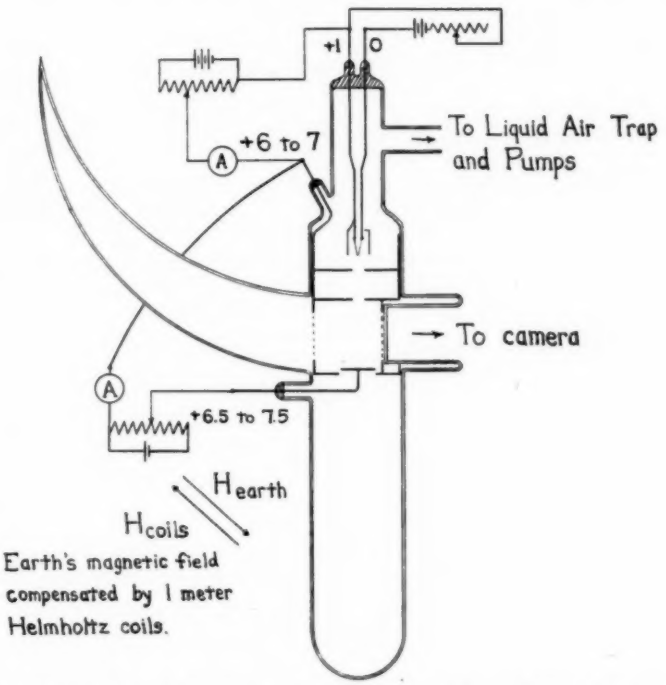

Fig. 1. Diagram of tube used for mercury vapor. The radiation produced by the beam of electrons was photographed through a quartz window by a camera with quartz lens and quartz Wollaston prism.

scattered resonance radiation diffusely fills the bulb. The portions of the discharge chamber which were cut away for the observation window and horn were covered with a very coarse grid of two or three fine platinum wires to reduce electrostatic effects. The wires by the window served as fiducial marks defining different sections of the beam.

The potential required to excite the $\lambda 2537$ line of mercury is 4.9 volts. However the next line $1S-2P$ is not produced below 6.67 volts, and since

the quartz observing system was opaque to this line, fields up to 7 volts introduced no spectroscopic complications even in the excitation of λ2537 as a two-stage process. In general, the field employed was around 6 to 7 volts. A few exposures at somewhat lower voltage showed no pronounced differences. It was found necessary to use an additional electrode at the bottom of the cylinder at a potential a few tenths of a volt positive to the cylinder. In this way the effect of space charge in the beam was partially neutralized. With proper care the beam could be limited to the geometrical projection of the diaphragms and extended for about 2 cm, well past the observation window. The current represented by the beam was of the order 5 to 20 μ-amp.

The beam was photographed by means of a camera with a quartz objective. Between the objective and the tube was mounted a large quartz Wollaston prism so oriented that one image represented the intensity of the radiation polarized with the electric vector parallel to the beam and the other perpendicular. Plate I illustrates several typical exposures. The plates were photometered and a rough estimate of the intensity ratio was made on the assumption of a gamma value of 0.8 for the plate characteristic. This value is probably a fair assumption for λ2537 and the type of development employed, although of course it cannot be considered as quantitatively correct. Exposures were usually of about two hours. With mercury it was necessary to compensate for the earth's magnetic field by a pair of large Helmholtz coils since the vapor is extremely sensitive to the depolarizing action of a field. Lead-in wires for the filament current of about 5 amperes were twisted together and every precaution was taken to eliminate stray fields. Nothing but platinum was used in the construction of the discharge chamber and heavy platinum wires extended well back to the tungsten seals. These precautions were not necessary with sodium as is shown by the behavior of the resonance radiation in fields of one gauss or less. The usual high vacuum technique was employed. The tube was well baked at 360°C and, upon cooling, a drop of metal, after several distillations, was condensed in the bottom. The pressure on the fore-pump side was below that readable on a McLeod gage.

In order to be certain that the beam in mercury vapor represented true electron impacts and was not resonance radiation excited by the 2537 radiation produced between the filament and the diaphragm system, a weak magnetic field, perpendicular to the beam, was introduced by a second pair of Helmholtz coils. The beam was bent into a circular arc well out of the geometrical projection of the filament, proving the effect to be due to electrons.

Sodium. Since the beam in sodium is visible, photographic difficulties may be eliminated. The observing device consisted of a quartz wedge and nicol prism oriented for the production of fringes. No polarization was observed although a polarization of 2 percent could have been readily detected. It does not seem likely that the vapor pressure at 150°C was sufficient to have caused any depolarizing action by atomic collision. This experiment, which was made about a year ago, is an independent confirmation of the recent work by Kossel and Gerthsen.[3] They were

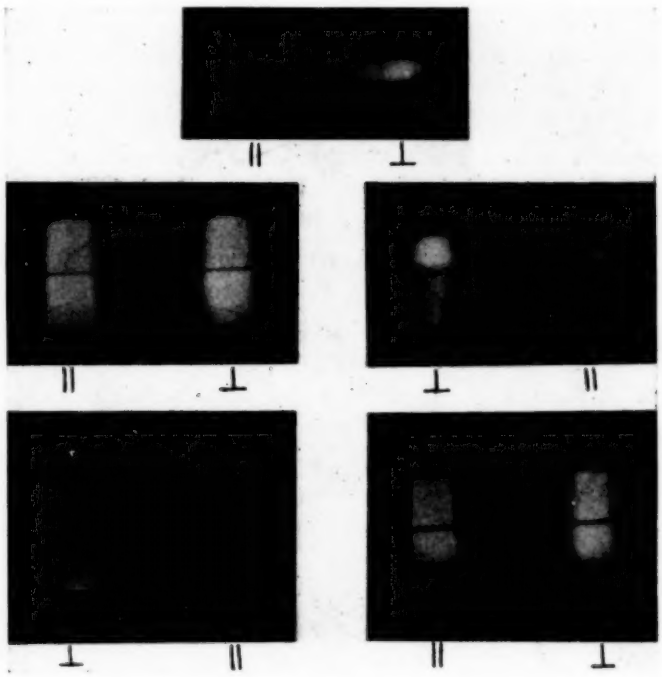

Plate 1. At −18°C the beam of λ2537 radiation from mercury vapor is sharply defined by the geometrical projection of the diaphrams limiting the beam of electrons. The width of the beam is about 3 mm. The ends of the beam are limited by the re-entrant quartz tube and window. The component of the radiation polarized with the electrical vibration perpendicular to the electron beam is about twice as intense as the parallel component. Densitometer measurements on the original negatives were made at corresponding points of the two images as determined in reference to the wire marker reproduced as a black line. Since the difference in densities of the two images is only 0.2 to 0.3 the contrast is not striking. The upper photograph was made with a tube of different design and considerable scattered radiation from the hot wire is present.

led to the experiment by theoretical considerations quite different from those proposed above. Thus, according to their theory, the predicted

[3] Kossel and Gerthsen Ann. d. Physik, 77 pp. 273-86 (1925).

polarization is about 60 percent for 3 volt impacts. Since two lines are emitted, with $\Delta j=0$ and $\Delta j=1$ respectively, in the intensity ratio 1:2 we should expect, on the basis of Sommerfeld's quantum numbers, a polarization of 20 percent.

Mercury. With mercury vapor in the absence of any applied magnetic field, we find a polarization of about 30 percent with the greatest intensity of the electrical vibration having its direction perpendicular to that of the electron beam. The polarization therefore is in the opposite direction to that predicted by the theory outlined above and by that of Kossel and Gerthsen.

Using a uniform magnetic field of about 3 gauss, the following observations were made with mercury vapor. (1) A field parallel to the direction of motion of the electrons produced no effect perceptibly different from that without the field. (2) When the field was perpendicular to the direction of motion of the electrons, the radiation emitted along the field was unpolarized and that emitted perpendicular to both the electron beam and the field showed a polarization of 13 percent, the maximum intensity of the electric vibration being perpendicular to the electron beam.

These effects with the field are in the proper direction if the field produces a Larmor precession in the excited atom so that it radiates with the same distribution of polarization and intensity as it would in the absence of the field, but with the atom rotated through some angle determined by the time of excitation and the precessional velocity.

BUREAU OF STANDARDS,
WASHINGTON, D. C.
September 20, 1925.

PHOTO-IONIZATION AND RELATIVE ABSORPTION PROBABILITIES OF CAESIUM VAPOR*

By F. L. Mohler, Paul D. Foote and R. L. Chenault

Abstract

Measurement of photo-electric ionization in gases.—The method[1] depends upon the partial neutralization of the negative space charge around a hot wire cathode by the ions produced by radiation. The change in thermionic current is proportional to the product of the intensity of radiation, number of atoms of vapor per unit volume, the Einstein probability coefficient B_ν, a quantity R representing the number of electrons released by a single ion and certain numerical factors relating to the geometry of the apparatus. The magnitude of R is of the order 10^4 to 10^6 depending upon the vapor pressure and other characteristics of the tube. Under constant experimental conditions and when the change in current upon illumination is small compared to the total thermionic current, R assumes a definite fixed value. Hence the change in current per unit intensity at different frequencies gives relative values of B_ν.

Absorption probabilities.—The absorption probability coefficient of a caesium atom for wave-lengths shorter than the $1s$ limit λ3184 decreases much more rapidly with decreasing wave-length than follows from the λ^3 law of Milne or the λ^4 law of Kramers although the latter is satisfactory for x-ray absorption. The theory of Becker is in good agreement with the data for the range λ3050 to 2700. An empirical relation of the form $B_\nu = B_{\nu_1} e^{-a(\lambda_1 - \lambda)}$ where $\lambda_1 = 3184$, appears to represent the experimental values throughout the observed range λ3184 to 2600. Vapor pressures investigated extended from 5 to 500 bars.

Photo-excitation.—Photosensitivity curves between λ3900 and the limit show that appreciable ionization is produced only at the wave-lengths corresponding to the principal series lines, the resolved effect of the individual lines being measurable from $1s-4p$ to $1s-9p$ with indications of further peaks, the definition of which was limited by the resolving power of the monochromator. The ionization is due to the production of excited atoms which are ionized by atomic collision. The relative magnitude of the photo-ionization at the different lines is in accord with the theory based upon the above hypothesis.

RECENTLY[1] two of the authors described a new method for detecting the photo-electric ionization of a gas, which was applied to the measurement of the photo-electric effect in caesium vapor. The vapor was contained in a two-electrode quartz tube. A hot wire cathode was enclosed by a cylindrical electrode having a gauze end through which the exciting radiation was transmitted. Conditions were adjusted to be

* Published by permission of the Director of the National Bureau of Standards, U. S. Department of Commerce.

[1] Foote and Mohler, Phys. Rev. **26**, 195-207 (1925).

such that the electron current without illumination was limited by space charge and the formation of ions by the radiation tended to break down the space charge and to produce an increase in thermionic current. This effect is greatly accentuated by the imprisonment of the ions, as a result of which a single ion may be responsible for the emission of 10^5 or more electrons. The photo-ionization of caesium vapor was found to be a maximum at the limit of the principal series, λ3184. Photosensitivity was also observed at longer wave-lengths which was attributed to the ionization by interatomic collision of excited atoms.

The present paper is a continuation of this work. The tube was operated at temperatures ranging from 130 to 230°C. With an applied voltage greater than the ionization potential, a current of about 10^{-2} amp. was obtained. As indicated by the voltage at which ionization occurred the actual potential difference was about 1 volt greater than the applied value. For the photo-ionization measurements the applied voltage was zero, and the current was 2×10^{-5} amp. which agrees with the value computed from the space charge equation when $V=1$ volt. The thermionic current was balanced out by a potentiometric circuit, and the galvanometer sensitivity was increased as desired for the radiation measurements. Under favorable conditions a sensitivity as high as 4×10^{-10} amp. per mm could be utilized. The increase in current due to the illumination, if small compared to the total thermionic emission, is proportional to the number of ions formed. With the potentiometric circuit, this increase in current is read directly from the galvanometer deflection.

The amalgam mirror of the Hilger quartz monochromator (aperture $F/7$ at λ3000) was replaced by a sputtered platinum surface, the reflection coefficient of which is known. As light sources were used a 400 watt concentrated filament Mazda lamp, a quartz mercury arc and a tungsten lamp with a quartz window, containing mercury vapor to suppress volatilization of the filament. The sources were focused on the entrance slit of the monochromator while no lens was employed between the exit slit and the ionization tube.

Galvanometer drift and slight changes in photosensitivity of the tube, in part due to temperature variation, were greatly reduced by using storage batteries for all the electrical circuits and by adjusting the currents several hours before obtaining the final measurements. Three galvanometer readings were observed at each monochromator setting, with the illumination on, off and on; a series of such measurements were made for a range of wave-lengths and then repeated in the reverse order. In general, slit widths of 0.005 inch were used with the Mazda lamp in

the range λ3900 to 3100 while slits as wide as .04 inch were necessary with the quartz tungsten lamp at the shorter wave-lengths near λ2800.

Data showing the relative values of the ratio of photo-electric ionization to light intensity as a function of the wave-length are of especial interest in connection with the theoretical interpretation of ionization by radiation. Unfortunately the intensity of the radiation incident upon the ionization tube was insufficient for a direct evaluation by means of a thermopile. Dr. Coblentz very kindly made several thermopile measurements for us with the mercury arc as source, but only two or three of the strongest ultraviolet lines could be detected with certainty and the galvanometer deflections for these were less than 1 cm. Intensity values were therefore obtained by computation using the thermopile data merely as a check.

The radiation flux $J_\lambda \Delta\lambda$ with the tungsten-quartz lamp as source was assumed proportional to the intensity of a gray body at 3000°K, times the reflecting power of the platinum mirror, times the reciprocal of the dispersion factor of the monochromator. With the Mazda lamp, these values were further multiplied by the transmission coefficients of a sample of glass from a similar lamp.

Experimental Data

Table I illustrates the experimental conditions under which the photo-ionization measurements have been made. The vapor pressures are computed from data by Langmuir and Kingdon.[2] At the four higher temperatures both tungsten lamps were employed and in the range λ3600 to 3100 readings were made with a 0.005 inch slit at 10A intervals. The Mazda lamp alone was used at the lower temperatures and fewer measurements were obtained.

Table I

Conditions for photo-ionization measurements
(Mazda lamp illumination)

Temp.	Pressure	Current at 3200A slit .01 inch	slit .005 inch
230°C	500 bars	19.5×10^{-8}amp.	4.7×10^{-8}amp.
202	170	24.2	5.7
182	74	....	2.9
162	29	9.0	2.2
149	15	6.7	...
134	9.7	4.2	...
128	5.0	1.6	...

Fig. 1 shows the photosensitivity, corrected for an equal energy spectrum, as a function of the wave-length, for the temperatures 182° and

[2] Langmuir and Kingdon, Proc. Roy. Soc. **107A**, 61-79 (1925).

230°C. Table II gives some of the data for these curves as well as the relative values of the incident radiation flux. The last two columns tabulate the heights of the separate peaks in the curves of Fig. 1 from λ3880 to 3310 and the points on the continuous curve for shorter wave-lengths. These values are the directly determined means of the experimental data. There is a small but perceptible difference between the two curves of Fig. 1. Curves for 162° and 202° resemble closely that for 182°, as do also the less accurate data for the lower temperatures.

TABLE II

Photosensitivity and radiation flux for three sources

Flux for tungsten lamps relative to λ3184 as unity; mercury arc relative to λ3130 as unity. Data of Pflüger (Kayser's Handbuch) are chosen since they give the same ratio of intensities at 3130 and 2537 as our thermopile readings.

Source	Wave-length	Relative flux $J_\lambda \Delta\lambda$	Sensitivity for equal flux 182°C	230°C
Mazda lamp	3880A	28.0	....	.006
	3610	12.4	.038	.051
	3480	7.9	.069	.092
	3400	5.4	.092	.129
	3350	4.0	.156	.216
	3310	3.1	.20	.27
Quartz-tungsten lamp	3300	1.64	.18	.28
	3280	1.47	.25	.33
	3260	1.35	.37	.41
	3240	1.25	.54	.54
	3220	1.15	.76	.72
	3200	1.05	.93	.90
	3180	.95	1.00	.97
	3160	.85	.92	1.00
	3140	.79	.84	.97
	3120	.73	.73	.86
	3100	.67	.69	.75
	3060	.57	.52	.60
	3020	.47	.40	.48
	2980	.38	.33	.40
	2940	.32	.28	.33
	2900	.26	.19	.27
	2860	.21	.15	.21
	2820	.16	.14	.18
	2780	.13	.12	.17
Mercury arc		Thermopile		Pflgüer
	3130	1.0	.78	1.0
	3030	.27	.34	
	2970		(.35)	.3
	2650		.2	.2
	2537	.67	.42	.6

The measurements for wave-lengths greater than λ3300 may be shown to advantage on a much larger scale (Fig. 2). This figure includes data for 162° and 230°C and in the upper portion of the drawing a map of the principal series lines. The peaks coincide with the series lines within the precision of the monochromator setting; apparently the widths are

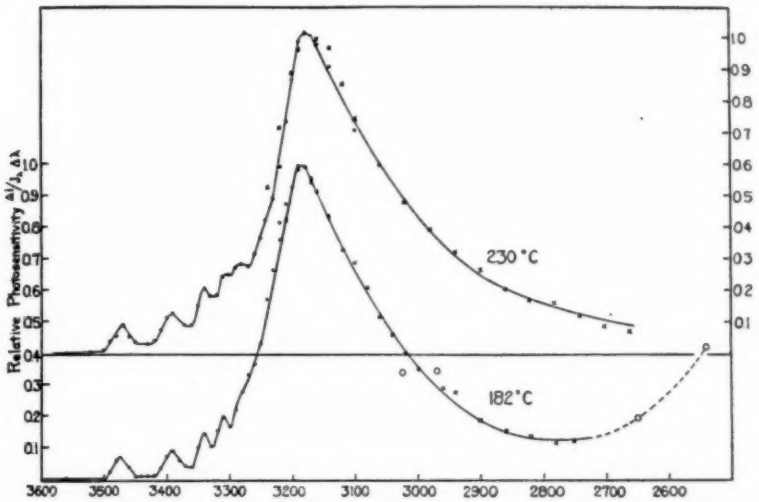

Fig. 1. Relative photosensitivity of caesium vapor corrected for an equal energy spectrum. The maximum sensitivity occurs at the limit 1*s* of the principal series.

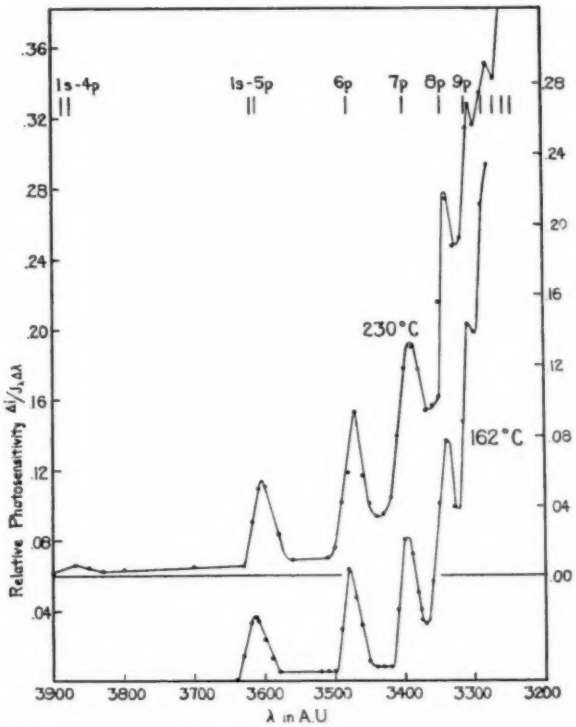

Fig. 2. Relative photosensitivity of caesium vapor on the long wave-length side of the photo-electric threshold. The peaks coinciding with the principal series lines are due to the ionization of excited atoms by interatomic collision.

determined by the resolving power of the instrument. Thus the observed effect for wave-lengths longer than λ3300 is largely if not entirely due to the separate lines. One may safely assume that in the range λ3300 to 3184 the curves show the unresolved effects of the closely-spaced higher members of the principal series.

Interpretation of Experimental Data

Direct photo-electric ionization. Let us consider the numerical relationship involved between the observed photo-electric current and certain atomic properties of the vapor. If I_ν is the intensity of isotropic radiation of frequency ν, we may define the quantity B_ν such that $B_\nu I_\nu d\nu dt$ is the probability that an atom in the normal state absorbs a quantum of radiation and becomes ionized in the time dt under the influence of this radiation.[3] Let a beam of radiation having the solid angle $d\omega$ be incident at the angle ϑ on an element dS of the vapor surface. The amount of energy falling upon dS in the time dt is therefore $I_\nu d\nu \cos\vartheta dS\, d\omega\, dt$. If k_ν is the mass absorption coefficient and ρ is the vapor density, the fractional amount of energy absorbed by the thickness dx is $k_\nu \rho dx/\cos\vartheta$. Hence

$$\text{Energy absorbed in time } dt = I_\nu d\nu\, dS\, d\omega\, dt\, k_\nu \rho dx \qquad (1)$$

This energy is also given by the product of (the number of atoms in the volume under consideration) × (the probability of absorption by a single atom) × (the correction for lack of isotropism of the beam) × (the energy of a quantum) as follows.

$$\text{Energy absorbed in time } dt = N\, dS\, dx \cdot B_\nu I_\nu d\nu dt \cdot (d\omega/4\pi) \cdot h\nu \qquad (2)$$

where N is the number of atoms per cm³. On equating (1) and (2) we find

$$k_\nu \rho / h\nu = B_\nu N/4\pi \qquad (3)$$

Eq. (3) therefore gives a simple relation between the mass absorption coefficient and the Einstein probability factor B_ν.

Let $E_\nu = J_\nu d\nu = J_\lambda d\lambda$ = the energy flux between ν and $\nu+d\nu$ in ergs per sec. per cm² surface of the vapor taken normal to the beam. Then at the depth x the flux is given by

$$E_\nu' = E_\nu \epsilon^{-k_\nu \rho x}. \qquad (4)$$

For the small values of $k_\nu \rho x$ concerned in the present work, on putting the energy absorbed $(E_\nu - E_\nu')$ equal to ΔE_ν this reduces to

$$\Delta E_\nu = E_\nu k_\nu \rho x. \qquad (5)$$

The number of quanta absorbed is $\Delta E_\nu / h\nu$ and if the absorption of each quantum results in the production of an ion, this is equal to the number

[3] See Milne, Phil. Mag. **47**, 209 (1924).

of ions produced per second per cm² of cross-sectional beam area and depth x. The total number of ions n, produced in the ionization chamber of volume $w(=x\times$cross section of beam) is therefore

$$n = E_\nu k_\nu \rho w / h\nu \tag{6}$$

Let i = number of electrons emitted by the hot wire per second when the current is limited by space charge, and Δi = increase in this number due to the presence of ions, then

$$\Delta i = Rn \tag{7}$$

where R by definition represents the number of electrons which a single ion is capable of releasing by partial neutralization of the negative space charge. The characteristics of this quantity will be considered below. On substituting the value of n from Eq. (6) and by use of Eq. (3) we finally obtain

$$\Delta i = (RE_\nu wN/4\pi)B_\nu. \tag{8}$$

The increase in current Δi, on illumination, is given by the galvanometer deflection. Theoretically E_ν could be evaluated absolutely by use of the spectrothermopile although with the sensitivity at our disposal the best that could be hoped for was a rough estimate of the energy over a very wide spectral range. Thus if R were known, an approximate estimate of B_ν in absolute value could be obtained. While this is a very indirect method of evaluating B_ν it would appear to offer greater possibilities than the direct determination of the absorption coefficient and the use of Eq. (3). For example Harrison's data[4] on sodium under dynamic equilibrium, as nearly as may be estimated from the tabulated measurements, indicate a mass absorption coefficient, on the short wave-length side near the limit, of $k_\nu = 3\times10^{-4}$ or an atomic coefficient $= k_\nu\rho/N = 10^{-18}$. Since Harrison and Slater present evidence that with the rapidly distilling vapor at the high temperatures employed there are about 50 times as many diatomic molecules as atoms, the consideration of this coefficient as an atomic constant is, of course, questionable; however, it may indicate order of magnitude. The physical process occurring in photo-electric absorption near the limit is the same for all alkalies so that caesium should have an atomic absorption coefficient of the same order of magnitude as sodium. At the highest pressure we employed, 500 bars, an absorption coefficient of 10^{-18} would necessitate a tube 900 cm in length for an absorption of 50 percent. The experiment, therefore, is not promising for observations under static equilibrium, whereas, by the photo-

[4] Harrison, Phys. Rev. **24**, 474 (1924); Harrison and Slater, idem **26**, 176 (1925).

electric method described, operation at much lower pressure, with a resulting increase in the relative concentration of monatomic vapor, is quite satisfactory.

We have attempted to evaluate R the efficiency factor of the tube. Measurement of the current produced by illumination when the filament is not heated should give the ion current plus the photo-electric emission from the filament, the latter being slightly negative to the cylinder. It was hoped that from measurements at different pressures, the second factor could be eliminated, but the results were not sufficiently reproducible. The data indicate that R is greater than 10^4 at the highest pressure employed and may be as large as 10^6 at lower pressures.

Kingdon[5] used a tube especially designed for the determination of R and in certain cases observed values as great as 300 times the mobility ratio of ions to electrons at low pressure, corresponding to 10^5 for caesium. He also found that R was proportional to the $-2/3$ power of the pressure. Using data in Table I of our earlier paper, one finds that Δi is proportional to $p^{0.4}$, and remembering that N in Eq. (8) is proportional to p, this gives R as proportional to $p^{-0.6}$, in fair agreement with Kingdon. The factor R besides depending upon the general geometry of the apparatus involves the recombinations which occur between the ions and electrons. With the weak fields employed for our work, it is very sensitive to changes in applied potential or space charge as altered by varying the filament temperature. The space charge may be appreciably affected by intense illumination and the resulting production of ions, especially at the higher pressures. If however, the value of Δi is not greater than possibly 1 percent of the total thermionic current i, the direct proportionality between Δi and E, as a variable is quite accurately fulfilled; that is, R remains a constant. This relation was carefully checked by use of wire gauze absorption screens and all of the observations recorded in the present paper are within the prescribed limit. One must finally consider whether or not R depends upon the frequency ν. The tube is sensitive to the production of ions and insensitive to electrons. All the ions are of the same type regardless of the radiation by which they are produced. The photo-electrons to be sure are ejected with a velocity dependent upon ν, but especially when present to only 1 part in 10^7, in order of magnitude, of the normal thermionic current i it seems impossible that R may be affected by small changes in ν.

Hence, according to Eq. (8), for Δi small compared to i and with constant experimental conditions, i.e., vapor pressure, temperature, filament

[5] Kingdon, Phys. Rev. **21**, 408-18 (1923); our R is equivalent to Kingdon's α.

temperature and applied potential, Δi is directly proportional to $E_\nu B_\nu$. Since $E_\nu = J_\nu d\nu = J_\lambda d\lambda$ or, considering the finite slit width, since $E_\nu = J_\lambda \Delta\lambda$ we have

$$\Delta i = K J_\lambda \Delta\lambda B_\nu \tag{9}$$

where K is a proportionality constant. The curves of Figs. 1 and 2 and the data in Table II represent relative values of $\Delta i / J_\lambda \Delta\lambda$ as a function of λ. Hence, the ordinates of the curves give the relative values of the probability coefficient B_ν for a ν value corresponding to the indicated λ. We believe that with especially designed apparatus the absolute values of B_ν may be obtained with some accuracy as indicated above, but for the present only relative values will be considered.

Since B_ν is an atomic constant, it should be independent of the pressure. This is qualitatively confirmed by the geometrical similarity of the two curves of Fig. 1 and several other curves not here reproduced. There are no data available in the literature for direct comparison. The lower curve shows an apparent increase in photosensitivity between λ2700 and 2500. The evidence is based chiefly on the measurements with the mercury line λ2537. Lawrence has suggested to us that this increase may arise from ionization of caesium molecules, an explanation consistent with his results for potassium vapor.[6] Another possibility is that merely a trace of mercury was present with the cycle of phenomena: absorption of λ2537; excited mercury atom; collision of the second type; highly excited caesium atom; completion of ionization by collision. While the usual precautions were taken to exclude mercury by baking the apparatus, etc., a small amount in the caesium could not have been completely removed by distillation. Spectroscopic examination of the vapor in a discharge at 10 volts failed to show any mercury lines, but prominent lines of rubidium and potassium were observed. These impurities could not have been present in a concentration sufficient to have affected our data. The caesium chloride from which the caesium was prepared by distillation in the presence of calcium was supposed to be fairly pure. Several fractional distillations in vacuum were made at low temperature which should have increased the purity since both potassium and rubidium have one fifth the vapor pressure of caesium at 250°C. Finally the percentage impurity present in the metal is reduced in the vapor by at least the factor 5 on account of the vapor pressure ratio. No evidence for either of these impurities was detected in the photosensitivity curves which, with an appreciable impurity, should have shown increased sensitivity at the corresponding principal series limits.

[6] Lawrence, Phil. Mag. **50**, 345 (1925).

In the x-ray range B_ν is fairly well known empirically as a function of ν or of λ. Referred to a particular x-ray level it is a discontinuous function equal to zero for wave-lengths greater than the absorption limit and is approximately proportional to λ^4 for shorter wave-lengths. Various attempts have been made to derive theoretically the form of the B_ν curve, notably by Kramers,[7] Milne[8] and Becker.[9] For an isotropic radiation field they find the relation between the probability of absorption of a quantum $h\nu$, resulting in ionization, and the chance of recombination of an ion with an electron of velocity v where ν and v are related by the photo-electric equation

$$\tfrac{1}{2}mv^2 = h\nu - h\nu_1 \tag{10}$$

ν_1 being the limit of the absorption series. The chance of recombination may be expressed in terms of the "effective collision area" q for an encounter resulting in recombination. The general relation between B_ν and q is

$$B_\nu/q = (\nu-\nu_1)/\nu^3 \times \text{constant.} \tag{11}$$

By the introduction of rather speculative assumptions as to the law of recombination, the following results are obtained. Kramers finds B_ν proportional to ν^{-4} or to λ^4. Milne's work leads to a proportionality between B_ν and ν^{-3} or λ^3 in which he excludes its applicability to x-rays, although the argument for this is by no means apparent.[10] Becker derives the relation

$$B_\nu = \frac{1}{(\nu-\nu_1)\nu^3}\left[1-\frac{(\nu-\nu_1)^2}{4\nu_1{}^2}\right] \times \text{constant.} \tag{12}$$

Eq. (12) is not applicable near the limit since it becomes infinite for $\nu=\nu_1$. Fig. 3 shows the form of these three theoretical relations, expressed by B_ν as a function of λ, together with our experimental values. The λ^3 and the λ^4 laws entirely fail in representing the data but satisfactory agreement with Becker's equation obtains in the range $\lambda 3050-2700$. An empirical relation of the form $B_\nu = B_{\nu_1} e^{-a(\lambda_1-\lambda)}$ where $\lambda_1 = 3184$, and B_{ν_1} is the value of B_ν at this wave-length, represents the observations in the range $\lambda 3184-2600$. If the data by Harrison on the absorption of the mixture of sodium atoms and molecules at high pressure are converted into relative B_ν values by use of Eq. (3) the general shape of curve ob-

[7] Kramers, Phil. Mag. **46**, 836-71 (1923).
[8] Milne, Phil. Mag. **47**, 209-41 (1924).
[9] Becker, Zeits. f. Phys. **18**, 325-43 (1923).
[10] Milne loc cit. p. 229.

tained resembles our measurements, certainly in preference to a third or fourth power relation.

For the spectral range λ3050 to 2700 the second term in brackets in Eq. (12) is negligible. Hence on combining this expression with Eq. (11) one finds

$$q=\frac{\nu^3}{\nu-\nu_1}B_\nu \times \text{const.} = \frac{\text{const.}}{(\nu-\nu_1)^2}$$

and by Eq. (10)

$$q=\text{const.}/\nu^4=\text{const.}/V^2 \qquad (13)$$

where V represents the velocity of an electron expressed in volts. This law is consistent with our observations between 0.15 and 0.5 volt. For

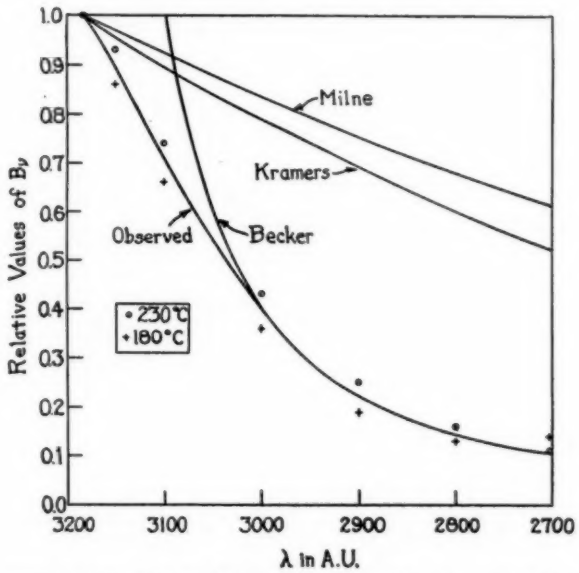

Fig. 3. Observed absorption probability of the caesium atom as a function of λ and graphs of the theoretical relations derived by Milne, Kramers and Becker.

lower voltages there is a wide departure. Eq. (13) is the Thomson law of recombination and cannot apply at low speeds since q must satisfy the condition that in Eq. (11) B_ν is finite when $\nu=\nu_1$.

Photo-ionization by line absorption. The observed relative sensitivity for direct photo-electric ionization, on the short wave-length side of the limit, and indirect ionization at points corresponding to the principal series lines depends upon the resolution of the monochromator. If both entrance and exit openings are doubled, the width of spectrum transmitted and the energy flux at each point in the exit slit are approximately doubled. When the vapor absorbs a continuous band the energy avail-

able for photo-electric ionization is therefore multiplied by four. At λ3200, the principal series lines are so close together that roughly the absorption may be considered as continuous so that even here the four-fold change in sensitivity should be expected, as illustrated by the data in Table I. If the absorption line is narrow compared to the slit width and lies in the spectral region corresponding to the first few terms of the principal series where the monochromator may differentiate definitely between the effects due to the adjacent members, doubling both slits approximately doubles the sensitivity of the tube. That is, the increase in heterochromatism of the beam produces no effect since the absorption is selective. At the low pressures employed, the absorption lines are very narrow so by decreasing the slit width the ordinates on the long wave-length side of a photosensitivity curve, such as Fig. 1, may be increased relative to those on the short wave-length side. Theoretically this process could be continued until the slits and absorption lines were of comparable width. The significance of the curve in the transitional region between these two conditions is therefore quite indefinite.

Table III shows the relative sensitivity of the tube at wave-lengths corresponding to the six principal series lines $1s-4p$ to $1s-9p$, a spectral region, except possibly for the last line, which is outside of the transition

TABLE III

Photo-ionization by line absorption
(Relative sensitivity at absorption lines)

Temp.	$1s$—$4p$ (3880)	$1s-5p$ (3611)	$1s-6p$ (3480)	$1s-7p$ (3400)	$1s-8p$ (3350)	$1s-9p$ (3314)
230°C	.1	.62	1.0	1.30	2.08	2.5
203	.12	.64	1.0	1.38	1.90	2.5
182		.62	1.0	1.24	2.00	2.5
161		.66	1.0	1.23	2.00	2.8
149		.70	1.0	1.36	1.98	3.3
134		.60	1.0	1.43	1.67	2.6
128		.60	1.0	1.15	1.32	1.9

stage mentioned above. The small corrections for dispersion of the monochromator have been removed from these values since the lines are narrow compared with the slit width. The numbers represent the relative heights of the observed peaks measured from the axis of zero sensitivity thus neglecting the small effect due to scattered radiation. While the lines are somewhat superposed, the sensitivity contributed by one line to the *observed peak* of a neighboring line does not become appreciable for wave-lengths greater than $1s-9p$. Some change in relative sensitivity at the peaks for different temperatures is indicated but for the

pressure range represented, 5 to 500 bars, it is surprising to find the data so nearly constant.

The observed photo-ionization arises from a type of multiple excitation. From the data presented in the first paper, it was concluded that atoms in an excited state having a low ionization potential as a result of line absorption, may be ionized by collision with other atoms. The values given in Table III permit an extension of this idea. The probability of ionization depends upon at least three factors: (1) probability of absorp-

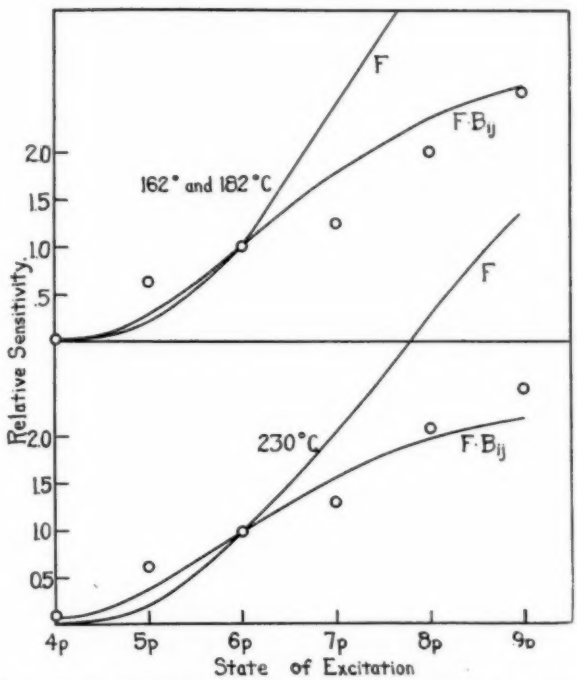

Fig. 4. Observed photosensitivity, represented by circles, of the caesium atom on the long wave-length side of the 1*s* limit. The curve FB_{ij}, except for a small variable and unknown factor, is the probability for the occurrence of the physical process responsible for the sensitivity.

tion, (2) chance that the kinetic energy of collision is sufficient to complete ionization and (3) chance that the excited state persists or is passed on by resonance until collision occurs.

The first factor depends upon the probability B_{ij} that the atom in the normal state i absorbs a quantum and passes over to the state j. These probability factors are unknown for the caesium lines here concerned but Ladenburg[11] has shown that the principal series of the alkalies are much

[11] Ladenburg, Zeits. f. Phys. **4**, 451-68 (1921).

alike in this respect so we may use the data by Harrison[12] for the relative probabilities in sodium. The chance of ionization by collision from an excited mp state may be estimated roughly by use of the kinetic gas theory. In the earlier paper this factor was designated by F. The third probability is unknown but is nearly unity at higher pressures. Fig. 4 shows the relative, observed photosensitivity at the successive lines, plotted as circles, and relative values of F and FB_{ij} for two temperature ranges. Qualitatively the agreement is excellent.

It is of interest that these experiments on the long wave-length side of the photo-electric limit yield a map of the principal series somewhat similar to an emission spectrum, yet no emission is taking place; in fact the sensitivity depends upon the suppression of the emission.

The authors desire to thank Dr. Sebastian Karrer of the Fixed Nitrogen Laboratory for lending them the quartz monochromator.

BUREAU OF STANDARDS,
WASHINGTON, D. C.
October 5, 1925.

[12] Harrison, Phys. Rev. **25**, 768-82 (1925).

LAWS GOVERNING THE PULLING OF ELECTRONS OUT OF METALS BY INTENSE ELECTRICAL FIELDS

By R. A. Millikan and Carl F. Eyring

Abstract

Current from thoriated tungsten filaments in vacuum, due to radial fields of up to two million volts per cm.—Three filaments were tested, each .00123 cm in diam. and suspended under tension in the axis of a copper cylinder of 1.6 cm diam. From the dimensions, the radial field at the surface of the filament was 228 times the applied potential difference. The electron currents pulled from the tungsten by the high fields (field currents) rise steadily from 10^{-12} to 10^{-3} amp. as the field is increased from about 400 to 1100 kv/cm. In the dark, luminous spots were seen on the anode, indicating that these currents come from a few active surface spots. The field current (for a given voltage) depends on the value of the maximum field current previously drawn from it (conditioning current), being reversibly reproducible below the conditioning current. The higher the conditioning current, the lower the field current. A previous heating to high temperatures (2400°C) decreases the field current and also decreases the slope of the current-voltage curve. Both effects (current and heating) show fatigue. *Variation with temperature of the filament, to* 800°C. The field currents are completely independent of temperature up to 700°, but a temperature of 800° increases the currents due to a given field when this is sufficiently large, by a factor which is roughly independent of the current (10^{-8} to 10^{-4} amp.). *Electron theory.* In explanation of these results, it is suggested that the field currents are due to conduction electrons pulled from minute peaks on the surface, the fatigue effects of both current treatment and heat treatment being due to the rounding off of these peaks by positive ion bombardment or by temperature. Chemical changes may also alter the surface. The lack of dependence of field currents upon temperature furnishes strong evidence that most of the conduction electrons do not share in the energy of thermal agitation. The thermions, however, do share in this energy; they are presumably responsible for the Peltier and thermo-electric effects. In this theory it is assumed that conduction electrons follow the same sort of quantum laws in their escape from the solid as do atoms of a light element at temperatures far below the boiling point.

I. Introduction

THE experiments of Earhart,[1] Kinsley,[2] Hobbs,[3] Hoffman,[4] and Lilienfeld,[5] a previous investigation by one of us,[6] and the theoreti-

[1] Earhart, Phil. Mag. **1,** 147 (1901); Phil. Mag. **16,** 147 (1908).

[2] Kinsley, Phil. Mag. **9,** 692 (1905).

[3] Hobbs, Phil. Mag. **10,** 617 (1905).

[4] Hoffman, Verh. d. Deutsch Phys. Ges. **12,** 880 (1910); Phys. Zeits. **11,** 961 (1910); Zeits. f. Physik **4,** 363 (1921); Phys. Zeits. **13,** 480, 1029 (1912); Ann. d. Physik **42,** 1196 (1913); **52,** 665 (1917).

[5] Lilienfeld, Akad. d. Wiss. Leipzig, Ber. (Math. Phys. Kl) **62,** 31 (1920); Verh. d. Deutsch Phys. Ges. P. **11** (1921); Phys. Zeits. **20,** 280 (1919); Phys. Zeits. **23,** 506 (1922).

[6] Millikan and Shackelford, Phys. Rev. **15,** 239 (1920).

cal discussion of Schottky,[7] all indicate that electrons may be pulled out of metals by intense electrical fields. In particular the experiments of Hobbs, which were suggested by and carried out under the direction of one of the present authors, made possible the computations of the field strengths at which this effect begins to appear. Many years ago the first of us made these computations and then endeavored to check the values obtained by new experiments made with spherical electrodes about 1 mm apart in the highest obtainable vacuum. After continuing this investigation with many modifications intermittently for a considerable number of years it became evident that in a vacuum so high that the gas plays no further part in the discharge, the potential gradient at the metal surface necessary to obtain a discharge is exceedingly variable even for the same metal surface. The most recent of these results were published very briefly in 1920.[6] It was found that with clean untreated surfaces—two crossed tungsten wires, size No. 18, placed a small fraction of a millimeter apart—a first leak, as measured on a tilted electroscope, was obtained at a gradient of from 100,000 to 500,000 volts per centimeter. When heated to red heat and then cooled, these same surfaces gave a first leak at from 400,000 to 700,000 volts per centimeter. After heating to 2700°K the first leak was pushed up to 4,300,000 volts per centimeter and the first spark up to six million volts per centimeter. The present investigation is a continuation of this attempt to see just how far surface conditions control the field strength needed to pull electrons out of cold metals, and how "field-currents" depend upon field-strength, temperature, etc.

II. Apparatus and Method

Since we wished to make the distance between the electrodes of the order of a centimeter it became necessary to design the apparatus in a manner such that the field intensity at the surface to be investigated would be very large *because of the small radius of curvature of the surface* and such advance as we have here made has been due primarily to this condition. Accordingly a tungsten wire of .00123 cm diameter was placed at the axis of a copper cylinder of 1.625 cm diameter. From these dimensions the field strength F at the surface of the wire becomes

$$F = 228\ \phi$$

where ϕ is the difference in potential between the electrodes.

The tungsten wire W and the copper cylinder C were placed in a Pyrex glass tube as shown in Fig. 1. The wire is kept taut by a four-gram iron weight I, and is adjusted so as to be in the axis of the cylinder.

[7] Schottky, Zeits. f. Physik **14**, 80 (1923).

Two leads are connected to either end of the fine wire and then brought through a seal in the upper part of the tube. It is thus possible to send a current through the tungsten wire and thereby to heat it to any desired temperature. When the wire is heated to temperatures over 1100°K the iron weight is lifted by means of an electromagnet, *E*. With this arrangement one may keep the wire taut at low temperatures and yet be insured against its breakage at high temperatures.

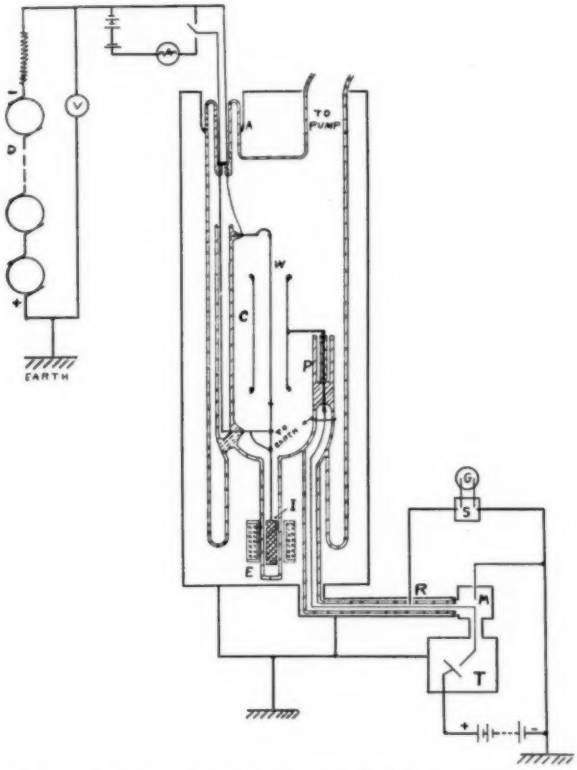

Fig. 1. Diagram of apparatus and electrical connections.

The cylinder is supported by a large tungsten wire that is sealed into the post *P*. This post has a glass sleeve to protect it from becoming coated with a deposit of copper when the cylinder is heated to bright redness in the process of denuding it of gases, otherwise the post might lose its insulating properties. An earthed guard ring is placed around the post *P* so that in case a charge should leak over the inside of the glass, none of it would reach the cylinder. The large tungsten wire passes through the seal in the post to the outside of the tube where it is joined to a copper wire leading to the tilted electroscope. A small

glass tube is sealed to the main tube in such a manner as to enclose this conductor which is then electrically shielded by covering the glass with earthed tin-foil.

An electric heater surrounds the main glass tube. The metal cylinder on which the heating coils are wound is grounded and thus the heater serves as an electric shield for the tube. A grounded guard ring is placed at A to keep the outside of the tube from becoming charged when a high potential is applied.

Direct current generators are used as the source of high potential, the maximum voltage available being 12000 volts. In series with the generators is placed a resistance of a million ohms to protect the apparatus should a short circuit be established between the wire and the cylinder. A Max Kohl electrostatic voltmeter V, calibrated in place, is used to measure the potential applied between the wire and the cylinder. A tilted electroscope T and a galvanometer G provided with a variable shunt are used to measure the "field-current" between the wire and the cylinder. The wire to the galvanometer is disconnected at R when the tilted electroscope is being used.

After properly baking the tube and charcoal trap during exhaust, a pressure of less than 10^{-6} mm of mercury was obtained. The tube would stand over night with liquid air on charcoal and mercury vapor traps, and then show no measurable pressure on the McLeod gauge (reading to less than 10^{-5} mm), and when the pumps were running, as was always the case during observations, the pressure was certainly far below 10^{-6} though no attempt was made in these particular experiments to measure it accurately. However, with the use of high speed mercury pumps, wide openings, charcoal in liquid-air, and precautions for denuding, the vacua here used were presumably as high as can now be produced.

At the proper time in the investigation the cylinder was heated to cherry red for from eight to twelve minutes by electronic bombardment. The bombarding potential was 2,000 volts and the bombarding current 100 milliamperes. The filament used as the source of thermions is stretched in a series of zigzags around and within half a centimeter of the cylinder. This part of the apparatus is not shown in the figure.

If the wire is to be heated simultaneously with the application to it of a potential, the apparatus used to furnish and measure the heating current is placed on an insulated stand. Using data published by Langmuir[8] the temperature of the wire is obtained from the value of the current in the wire and its diameter.

[8] Langmuir, Phys. Rev. **7**, 302 (1916).

Observations were taken on three specimens of thoriated tungsten wire. These pieces were from the same spool and, as explained above, had a diameter of .00123 cm. When a new wire was introduced the tube was opened up, the wire supplied, and the tube sealed up again.

III. Results

(a) *The rapid rise of "field-current" with increasing potential gradient and the reversibility of the process.* The wires will be numbered I, II, III, the numbers indicating the order in which they were investigated. Fig. 2 presents the data obtained for wire I which had received no heat treatment other than that involved in baking out the tube, but which had been "conditioned," as explained below, by a .42 milliampere "field-current" (the current between the wire and the cylinder due to

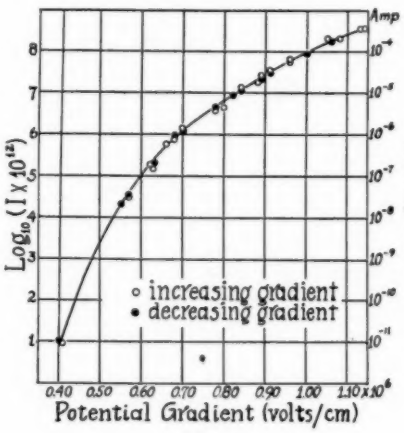
Amp
Log_{10} (I X 10^{12})
○ increasing gradient
• decreasing gradient
0.40 0.50 0.60 0.70 0.80 0.90 1.00 1.10 x 10^6
Potential Gradient (volts/cm)

Fig. 2

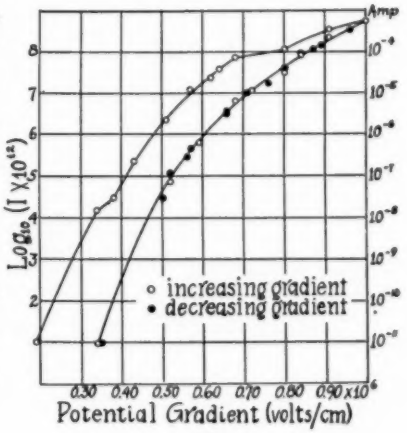

Fig. 3

Fig. 2. Variation of the logarithm of the "field-current" with potential gradient, for wire I, "conditioned" by a .42 m.a. "field-current."

Fig. 3. Variation of the logarithm of the "field-current" with potential gradient, for wire II, during and after "conditioning."

the pulling of electrons from the tungsten wire by the field alone). The figure clearly shows that *for a clean "field-current-conditioned" tungsten surface, but not heat-treated, the "field-current" increases more than ten-million-fold with a threefold increase of potential gradient,* i.e. *a gradient varying between .40 × 10^6 and 1.13 × 10^6 Volt cm. These data further show that for "field-currents" lower than the current which conditioned the surface the process is quite accurately reversible.*

(b) *Conditioning the surface by means of "field-current."* "Field-currents" drawn from the surface for the first time, or for the first time after some sort of heat treatment, generally produce a permanent effect

upon the surface, a sort of fatiguing effect that makes it more difficult to pull out electrons thereafter. This is shown in Fig. 3 which presents, in the upper curve, the first observations taken on wire II. After pushing the current up to the maximum shown, the currents obtained with diminishing applied potential are all below the corresponding value on the first rising-potential curve. However, the curve then becomes nearly reversibly reproducible until the current is pushed up above its former maximum value, an operation that again lowers the "field-current" for a given gradient. When the emitting surface has once been "conditioned" by drawing from it a large field current, and is not then subjected to further conditioning by current or by heat, it seems

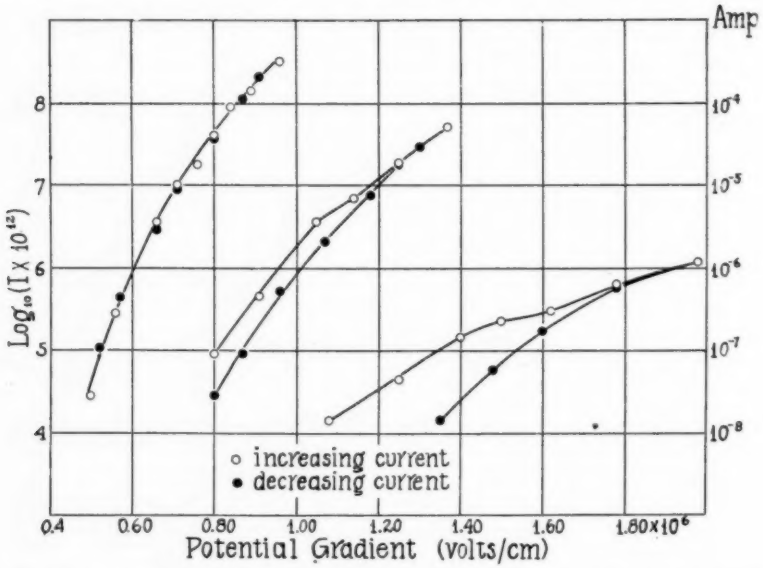

Fig. 4. The curves from left to right represent the data obtained on "current-conditioned" wires which have been heated to 700°K, 1300°K and 2700°K respectively.

to remain fairly constant and the current to become nearly reversibly reproducible (Fig. 3). But intense heat treatment modifies this condition as explained in connection with the data represented in Fig. 4.

Further, field-currents may be drawn for hours at a time without changing appreciably the "critical" potential gradient[9] except in the case of surfaces which have undergone intense heat treatment, and in this case the change due to the heat treatment does not appear to be permanent.

[9] In what follows, "critical" gradient is the potential gradient needed to produce a "field current" of 9.7 10^{-12} amp.

In one case a gradient of 1.7×10^6 v/cm applied to a surface which had been subjected to extreme heat treatment produced what we shall speak of as a rupture of the surface, for the "field-currents" increased slowly until this gradient was reached and then suddenly jumped up a thousandfold. Two definite spots on the anode opposite the regions of rupture appeared for the first time and these regions gave off nearly the whole of the current, for only two spots could be seen on the outer surrounding cylinder. Not only was the current for a given gradient increased, but the "critical" gradient was changed from 0.74×10^6 to 0.48×10^6 v/cm. This observation was made on wire III. No similar effect was observed on the other wires.

(c) *Conditioning the surface by heat treatment.* The effect produced by heating the wire is so dependent upon the way the impurities on the surface respond to different temperatures, that we shall divide the results of heat treatment into a number of parts, using the temperature range as the criterion of division.

TABLE I

Wire	"Critical" gradient[9] before baking	"Critical" gradient[9] after baking	Maximum temp. of baking
I	0.48×10^6 v/cm	0.37×10^6 v/cm	360°C
I	0.40	0.38	420°C
III	0.40	0.34	420°C

Long baking of the whole tube at 400°C reduced very slightly the critical potential gradient of a "field-current-conditioned" wire, this in spite of the fact that no change ever took place when the tube stood over night, or for a number of days, provided the vacuum was maintained during this time. The small, but apparently real, change with baking is shown by the data of Table I.

TABLE II

Conditioning "field-current"	"Critical" gradient after "field-current" conditioning (before heating)	"Critical" gradient after "field-current" conditioning (after heating)	Temperature	Total time of heating after conditioning
0.70 m. a.	0.41	0.32	900°K	10 min.
0.24	0.41	0.38	900	15
0.24	0.41	0.41	900	10
0.24	0.41	0.24	1100	5
1.05	0.40	0.27	1100	15
		0.24	1100	30
		0.22	1100	45
		0.21	1100	60
		0.22	1100	90

Heating wire II at 900° to 1100°K largely reduced the "critical" gradient of a "current-conditioned" surface. The "critical" gradient was re-established, however, by the "current-conditioning" process; in

fact the phenomenon is roughly reversible, but becomes less pronounced with continued treatment as may be seen from a consideration of the data of Table II.

The effect of raising the tungsten wire to a very high temperature is to increase markedly the critical gradient. This is shown in Table III. It checks a result previously found by Millikan and Shackelford (l. c.). This increase in critical gradient with intense heat treatment is not permanent but disappears on long standing as though the surface underwent slow chemical change.

TABLE III

Temperature	Total time of heating at the particular temp.	Resulting "critical" gradient
1100°K	10 min.	0.39×10^6v/cm
1300	10	0.39
1500	10	0.31
	25	0.26
	40	0.29
1700[10]	20	0.27
1900	10	0.57
	25	0.46
	40	0.34[11]
	55	0.61
1800	15	0.46
	30	0.42
	45	0.68
2300	10	0.74

(d) *Slope of "field-current"-gradient curve a function of "critical" gradient.* The rate of increase of the "field-current" with the potential gradient is large when the "critical" potential gradient is small and vice versa. This is clearly shown in Fig. 4. It is also an observation which had been made previously by the first of the authors. Further, the higher the "critical" gradient, which corresponds to a higher temperature in the heat treatment, the less the constancy and the less the reversibility of the field-current-gradient curves. This is shown clearly in Fig. 4.

(e) *The "field-currents" in general have their origin in a few minute surface spots.* For small currents, less than 10^{-6} amperes, and for corresponding potentials less than 4000 volts, the tube remains perfectly black as viewed in a darkened room. (Currents lower than these may produce a luminous effect if the potential is sufficiently high.) For larger currents luminous spots begin to appear on the inner surface of

[10] This temperature and those below it may be too high by 100° to 200°.

[11] This decrease in critical gradient at 1900°K is probably due to thorium which first comes to the surface at this temperature and on continued heating evaporates from it (see Langmuir, Phys. Rev. *22*, 357 (1923)).

the cylinder and fluorescent spots to appear on the glass wall directly out from the top of the cylinder. The spots must be due to streams of electrons shot out from active spots on the surface of the wire.

The patches of light on the cylinder are reddish-grey in color and as viewed through a direct-vision prism seem to have a continuous spectrum. However, this point should be tested more carefully in an apparatus designed for this purpose.

As the "field-current" increases the spots become brighter and new spots may appear. Some of the spots are fixed in position and for a given current, constant in luminosity; others are slightly changeable in position, and before a steady current state is reached, rather changeable in intensity, and even when the current appears steady there is some variation in these points.

TABLE IV

Wire	"Critical" gradient 300°K	900°K
I	0.415×10^6v/cm.	0.408×10^6v/cm.
	0.409	0.410
	0.417	0.408
	0.417	0.410
	0.413	0.410
		0.413
I	0.670	0.672
	0.672	0.670
	0.670	0.655
	0.655	
II	0.730	0.730
	0.741	0.736
	0.741	0.741
	0.741	

Sometimes in the "current-conditioning" process, very brilliant spots spring into existence. This is well illustrated by the action of wire II. An irregularity was noticed in the "field-current" and on looking into the tube a new spot was seen on the cylinder near its center. The spot was changeable in intensity but fixed in position. Its intensity slowly decreased and its luminosity became more steady. Thereafter, the current ceased to fluctuate. Another interesting case is that mentioned under (*b*) in connection with the study of wire III. The wire had been heat-conditioned and was giving off very small "field-currents" considering the magnitude of the potential applied. There were only slight traces of luminosity. The next small increase of potential produced the thousand-fold increase in current and two luminous spots had sprung into existence. They furnished practically all of the "field-current," which was rather unsteady. These spots were fixed in position,

but very changeable in intensity. The luminosity slowly decreased with continuous operation and the current settled into a more or less steady state.

(f) *The "critical" gradients and the "field-currents" are completely independent of temperature between 300°K and 1000°K.* Only data for the temperature of 900°K will here be recorded, although the effect of lower temperatures was investigated. Wires I and II were studied for this effect; the different "critical" gradients for the same wire are due to the previous conditioning process. The results are recorded in Tables IV and V.

TABLE V

Wire	Potential difference (volts)	Potential gradient (volts/cm)	"Field current" (amp.) 900°K	300°K	900°K	300°K
II	1730	0.39×10^{6}	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}
	2500	0.57	9.0×10^{-8}	9.0×10^{-8}	9.0×10^{-8}	9.0×10^{-8}
	3000	0.68	1.9×10^{-6}	1.8×10^{-6}	1.8×10^{-6}	1.8×10^{-6}
	3500	0.80	6.0×10^{-6}	6.0×10^{-6}	5.7×10^{-6}	5.7×10^{-6}
	4000	0.91	4.4×10^{-5}	3.9×10^{-5}	4.2×10^{-5}	4.1×10^{-5}
	4550	1.04	2.4×10^{-4}	2.3×10^{-4}	2.3×10^{-4}	2.3×10^{-4}
	4000	0.91	4.2×10^{-5}	4.2×10^{-5}	4.4×10^{-5}	4.4×10^{-5}
	3500	0.80	7.2×10^{-6}	7.1×10^{-6}	7.2×10^{-6}	7.2×10^{-6}
	3000	0.68	6.9×10^{-7}	6.3×10^{-7}	7.2×10^{-7}	6.9×10^{-7}
	2500	0.57	3.0×10^{-8}	3.0×10^{-8}	3.0×10^{-8}	3.0×10^{-8}
	1810	0.41	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}	9.7×10^{-12}
I	8450	1.92	9.0×10^{-7}	9.0×10^{-7}		

(g) *The "critical" gradients and "field-currents" with a tungsten wire at 1100°K.* (The wire is of a just-visible-red color.) The extent of the lowering of the "critical" gradient with this temperature depends upon the magnitude of the "critical" gradient at ordinary temperatures, *zero effect being observed for very low gradients and a considerable effect for higher gradients* (Table VI). The magnitudes of the "critical" gradients at ordinary temperature are, of course, the result of past treatment of the surface. Further, when the gradient is sufficiently high so that the field-currents at 1100°K are observably higher than those at 300°K, *the percentage of increase in current due to this 800° rise in temperature is quite as high for large currents (10^{-4} amperes) as for currents of one thousandth, or even one ten thousandth of this value, thus showing definitely that field currents and thermionic currents are not entirely independent phenomena,* (See §IV(f), below) *since otherwise their effects would be additive.* (See Table VII for the experimental data.)

IV. Interpretation of the Foregoing Results

(a) *Field currents due to "conduction" electrons.* The magnitude and the reversibility of the foregoing field-currents indicate that the electrons which are pulled out of a metal by a sufficiently intense field are the free or conduction electrons[12] of the metal, as Schottky[7] has pre-

Table VI

Wire	"Critical" gradient 300°K (volts/cm)	1100°K (volts/cm)
II	0.212×10^6	0.212×10^6
	0.212	0.212
	0.214	0.213
	0.216	0.214
	0.215	
	0.317	0.310
	0.317	0.310
	0.315	
	0.450	0.358
	0.456	0.360
	0.458	0.364
	0.800	0.560
	0.800	0.561
	0.792	0.560
I	0.402	0.315
	0.402	0.319
	0.399	0.322
	0.400	0.335
	0.399	0.335
	0.399	

Table VII

Wire	Potential difference (volts)	Potential gradient (volts/cm)	"Field-current" (amp) 300°K	1100°K	300°K
I	2600	0.59×10^6	1.2×10^{-8}	1.5×10^{-8}	1.5×10^{-8}
	3050	0.70	1.2×10^{-7}	1.4×10^{-7}	1.2×10^{-7}
	3500	0.80	6.0×10^{-7}	7.5×10^{-7}	6.0×10^{-7}
	4000	0.91	4.5×10^{-6}	5.4×10^{-6}	4.4×10^{-6}
	4400	1.00	2.1×10^{-5}	2.4×10^{-5}	2.1×10^{-5}
	4750	1.08	5.4×10^{-5}	5.9×10^{-5}	5.4×10^{-5}
	5000	1.14	1.0×10^{-4}	1.1×10^{-4}	1.0×10^{-4}
	4800	1.09	6.3×10^{-5}	6.9×10^{-5}	6.0×10^{-5}
	4200	0.96	1.2×10^{-5}	1.5×10^{-5}	1.2×10^{-5}
	3750	0.85	2.1×10^{-6}	2.7×10^{-6}	2.1×10^{-6}
	3200	0.73	2.4×10^{-7}	3.6×10^{-7}	2.4×10^{-7}
	3000	0.68	9.0×10^{-8}	1.5×10^{-7}	1.0×10^{-7}

[12] Conduction electrons are here defined as those that are responsible for the Ohm's law effects. They are free merely in the sense that there is no assignable lower limit to the e.m.f. that is required to set them streaming through the conductor.

viously assumed. For first, such large and constant electronic flows, of indefinite duration, would exhaust any other conceivable supply; second, the forces that are here involved are of an altogether different order of magnitude from those necessary to detach any bound electrons of which we have any knowledge. Thus the radiating potential of an atom which holds its outer electrons as loosely as does even sodium, for example, is about 2 volts, and by the application of these 2 volts, the electron is lifted through a distance of about 2×10^{-8} cm, i.e. from the normal position to its first excited position in which the diameter of the atom is about three times its normal diameter.[13] The lower limit to the field-strength, then, which would be required to pull off the electron of sodium from its normal position should be about $2/2\times10^{-8}$ $=100{,}000{,}000$ volts per cm. But these experiments show that field-currents begin to be obtained with the application of a field-strength (potential gradient) of less than 1/200 of this, or 500,000 volts per cm. No bound electron, then, of which we have any knowledge, i.e. no electrons which may be regarded as belonging to particular atoms, are held so loosely as to make it at all possible to consider them as the electrons which here escape. *We therefore regard our fields as reaching sufficiently into the metal to get hold of and pull out some of its conduction electrons.*

(b) *Effect of sub-microscopic irregularities.* The field-currents here studied consist of electrons which escape only from isolated points on the surface where the work function b has been enormously reduced by microscopic geometrical roughnesses, or chemical impurities, or both. The spotted character of the glow on the anticathode is sufficient proof that the discharge actually does come only from specially favored points on the cathode. Further, Schottky[7] has pointed out that it would require a field-strength of the order of 100,000,000 volts per cm merely to counteract (at a distance of 10^{-8} cm, where the electron may be assumed to start) the image-force due to an electron escaping *from a plane surface*; so that neither free nor bound electrons could possibly be pulled away from such a plane surface by the fields used in the foregoing experiments. We can, however, call upon geometrical roughnesses in the surface, of large dimensions in relation to molecular diameters, to reduce the required forces to the observed values. Chemical impurities may obviously assist somewhat in developing such weak points in the surface.

(c) *Conditioning effects of currents, presumably due to positive-ion bombardment.* The conditioning of the surface by means of strong field currents is presumably due to the battering down or rounding off by

[13] H. A. Stuart, Zeits. f. Physik **32**, 262 (1925).

positive-ion bombardment of the microscopic mountain peaks which act as the electron-emitting points of the surface.

The most sensitive means that we have of measuring extremely high vacua is the ionization manometer or Buckley gauge.[14] With this gauge electron currents of the order of milliamperes, such as are here obtained, produce enough positive ions to be easily measurable in the highest vacua that have ever been produced. The electron currents obtained in the present experiments come from a very few points and hence constitute extraordinarily dense electron streams, or pencils, following the direction of the lines of force at the surface. The positive ions formed in these pencils must in these very intense fields return along the same lines of force and bombard almost exclusively the points in the surface at which the electron pencils originate. This theory accounts very satisfactorily for the observed dimming of an anticathode spot with time, the sub-microscopic protuberance having been gradually beaten down into insensitiveness by this bombardment.

(d) *Conditioning effect of heat treatment due to geometrical and chemical changes in the surface.* The lowering of the critical gradient by general heat treatment (Tables I and II) is presumably due to the contamination of the surfaces by emitted gases, while the large increase in the critical gradient by the intense heat treatment of the emitting wire (Table III) is due to the rounding off of surface irregularities supplemented by the removal of surface impurities.

The rounding off of protuberances either by heat or by bombardment should produce all the effects shown in Fig. 4, namely, (1) increase of critical gradient with treatment since both kinds of treatment should reduce the protuberances; (2) decrease of rate of rise of field-currents with applied potential, since the contrast between the peak and its surroundings has been reduced by the treatment and the surface concentration of the field and also of the positive ion bombardment at the sensitive point has become less pronounced; (3) decrease of reversibility with increasing critical gradient, since heavy bombardment from a strong gradient ought to modify a surface more than would gentle bombardment from a weaker one. Indeed, with increasing critical gradient, i.e. increasing energy of bombardment, there is evidence that a definite rupture point of the surface is more and more nearly approached. When it is reached a disruptive discharge occurs by which the cathode may become pitted. This has been shown by point-to-plane discharges.

[14] O. E. Buckley, Nat. Acad. Sci., Proc. **2**, 683 (1916).

(c) *New proof that the energy of conduction electrons is independent of temperature.* The only preceding theoretical treatment[7] of field-currents assumes them to be composed of thermions escaping under their own energy of agitation through a boundary weakened by the external field. This conception is, we think, altogether irreconcilable with the foregoing data. Indeed, the entire independence upon temperature[15] of the field currents over a range of 700°C constitutes new and striking evidence that "equipartition" does not hold at all for the bulk of the conduction electrons in tungsten at ordinary temperatures. For when these conduction electrons escape as thermions, the law governing their escape is

$$i = AT^{n}\epsilon^{-b/T} \tag{1}$$

in which b is the work function of Richardson. The correctness of this thermionic equation is attested by a vast amount of experimental work. Now the effect of an externally applied field of such direction as to pull out electrons should be simply to weaken the effective value of the work function b and leave i in the foregoing equation varying as rapidly with T as it always does in thermionic experiments. *The fact, then, that in the present experiments i is not at all dependent upon T over a 700° interval means that the electrons pulled out by the fields here used are not thermions at all.* They might become such at high enough temperatures, but at temperatures up to 1000°K the electrons here pulled out can have no assistance at all from temperature in getting out, i.e., *they do not share in the thermal energy of agitation of the atoms.*

A little, but somewhat uncertain, evidence for this conclusion has been previously obtained by Davisson and Germer,[16] who could bring their two independent methods of measuring b into agreement within one per cent if the electrons within the metal had zero energy, while a discrepancy of 2.7 per cent appeared if the conduction electrons had the energy $3kT/2$. The evidence derived from the specific heats of metals is inconclusive, because the number of conduction electrons within a metal is entirely unknown. The present evidence, on the other hand, appears to be direct, accurate, and unambiguous for the non-participation of the great bulk of "field-current electrons" (conduction electrons) in thermal motion. There must of course be sufficient participation by a few conduction electrons to account for the Peltier and thermo-electric effects, but this is quite consistant with the quantum theory considerations here employed.

[15] Lilienfeld (l.c.) also reports such independence.
[16] Davisson and Germer, Phys. Rev. **20**, 300 (1922).

The energy of agitation of electrons within tungsten at ordinary temperatures must be altogether analogous to that of the atoms of solid elements at temperatures far below that at which Dulong and Pettits' law holds. The occasional atoms which escape from such a solid follow the Maxwell distribution law[17] and are in thermal equilibrium with the outside vapor, which obeys in all respects the gas laws, but the great mass of the atoms within the solid are devoid of energy of agitation and would be so found if a Maxwell demon could reach in and examine them as the field in the foregoing experiments reaches in and examines the state of agitation of the conduction electrons of the tungsten. *From the point of view here taken the conduction electrons are simply the lightest of the elements which, at ordinary temperatures, have taken on practically no kinetic energy, i.e , have zero specific heat, and which reach equipartition only at very high temperatures. Those of the conduction electrons which at any temperature have escaped from this zero-energy condition are the thermions.* If they carry the total atomic heat of the electrons and if this atomic heat follows the usual quantum law, then their number should increase, at low temperatures, with T^3. This would be consistent with Eq. (1).

(f) *Relations of field-currents and thermionic currents.* We have just seen that *at low temperatures* field currents bear no relation to thermionic currents and that their observed properties lead to the conclusion that the conduction electrons constituting them possess no agitational (temperature) energies at all. But as shown in Table VII, at 1100°K thermionic currents of measurable magnitude (10^{-12} amp.) begin to appear from tungsten and consequently the thermionic equation begins to show evidences of having a role to play in the character of the emission. Thus with increasing potential gradient, the value of the effective work function b is continually reduced and hence the value of the thermionic part of the current (the increase at 1100° over that at 300°) continually rises as is beautifully shown in Table VII so that it makes as large a percentage of the total current when the latter is 10^{-4} amperes (potential difference 5000 volts) as when it is 10^{-8} amperes (potential difference 2600 volts).

Quite similarly, as shown in Table VI, strong fields begin at this temperature to bring into evidence the thermionic part of the current when weak fields are unable to do so. In other words, when the temperature is reached at which the number of thermions escaping without external field is at all comparable with the number constituting the

[17] See Germer's recent proof that the Maxwell distribution law holds accurately for thermions escaping into a high vacuum, Phys. Rev. **25**, 795 (1925).

field current at what we have called the critical potential gradient, the decrease in b due to increasing field pushes up the number of emitted thermions (the electrons coming out in accordance with Eq. (1)) slightly faster than the increase in field pulls out field-electrons. Another way of saying this is that field currents are a less rapidly rising function of the field than are thermionic currents (those following Eq. (1) with b regarded as a function of the applied field F.)

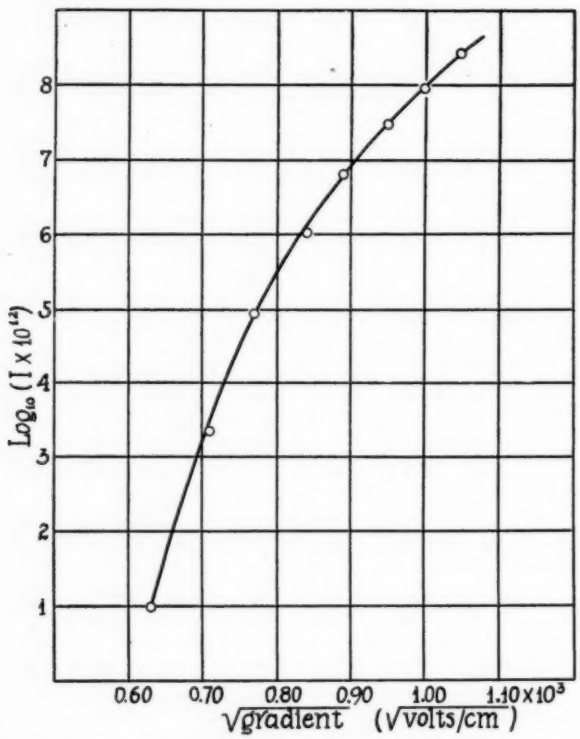

Fig. 5. Variation of the logarithm of the field current with the square root of the potential gradient.

A check on this conclusion may be obtained as follows: If the field currents were made up wholly of electrons, following Eq. (1) we could compute the relation between i and F if we knew how the effective work function b is diminished with increasing F. For sufficiently small values of F, where it is just beginning to influence b appreciably, it is possible to compute what sort of function of F the effective value of the work function is. For at a sufficient distance x_1 from the surface of the wire (a distance large compared to the surface irregularities) it is the image-force alone which must be overcome to cause the electron

to leave the surface. The value of this image force per unit charge is $e/4x_1^2$. Every electron must escape which reaches the distance x_1 at which $e/4x_1^2 = F$, i.e., at which $x_1 = \sqrt{e/4F}$. Now the total work necessary to bring an electron out to x_1 is the work b_0 necessary to bring it up to the point x_0 at which the image law begins to be valid plus the integral $\int_{x_0}^{x_1} (e/4x^2 - F)e dx$. That is, the work function is

$$b_0 + \int_{x_0}^{\sqrt{e/4F}} (e/4x^2 - F)e dx = b_0 + e^2/4x_0 - \sqrt{e^3F} + eFx_0$$

Since x_0 is very small (10^{-8} cm) the last term may be dropped while the first term is the total work necessary to bring the electron out *when there is no field*. Hence $b - \sqrt{e^3F}$ is the work function in the presence of an external field F and the thermionic equation becomes $i = AT^n\epsilon^{-(b-\sqrt{e^3F})/T}$. This equation shows that when T is constant and F alone varies $\log i \propto \sqrt{F}$. This equation should hold so long as all the escaping electrons are brought up to the point x_1 *by their own energy of agitation*. In other words, it should govern the increase in ordinary thermionic emission due to a relatively weak field F. Schottky[18] states that he has tested it for this case and found that the plotting of *log i* against $\sqrt{F}$ yields a straight line.

When, however, we plot for our cold wires log i against $\sqrt{F}$ *using the data given in Figs. 2, 3, or 4 we do not obtain a straight line but instead a curve continually concave toward the* $\sqrt{F}$ *axis* (see Fig. 5). *This means that our field currents do not rise as rapidly with increasing F as is demanded by the thermionic equation.* This is precisely the conclusion we drew from the data in Table VI.

All of our observed phenomena have now been rendered intelligible with the aid of the conceptions which we have herein used.

NORMAN BRIDGE LABORATORY OF PHYSICS,
CALIFORNIA INSTITUTE OF TECHNOLOGY,
October 25, 1925.

[18] Schottky, Jahrb. d. Radioakt. **12**, 203 (1915).

THE FIVE ALKALI METALS UNDER HIGH PRESSURE

By P. W. Bridgman

Abstract

Effect of high pressure on the melting constants, electrical resistance and volume of the alkali metals.—(1) *New data for Rb and Cs*, presented in detail elsewhere, are given in three tables. Then, since similar data have previously been obtained for Li, Na and K, the results of a comparative study of all five alkali metals under pressure are given and discussed. (2) *Melting constants.* The general character of the melting phenomena is the same for the alkali metals as for other substances; the melting curve continues to rise indefinitely with increasing pressure, with neither maximum nor critical point. Above 10000 kg/cm² there is a reversal of the normal melting points of Na and K, and a moderate graphical extrapolation indicates other reversals also, so that at high pressures we may expect a complete reversal of the order of normal melting temperatures, Cs being the highest and Li the lowest. The fractional change of volume on melting is the same within 25 percent for Na, K, Rb, and Cs, as is also the latent heat of melting per gm atom; for Li the values are only about one-fourth as large. (3) *Electric resistance.* K shows the greatest relative decrease of resistance with pressure above 1400 kg/cm²; Rb occupies electrically an intermediate position between K and Cs. The effect of pressure on the resistance of Cs is unique in that there is a minimum (at 4000 kg/cm²). This minimum seems to have no connection with the crystal structure of the solid, but will probably be shown by the liquid also at higher pressures. At low pressures Cs has the maximum negative pressure coefficient of resistance and at high pressures the maximum positive coefficient of all pure metals measured. At high pressures the curve of pressure coefficient of resistance of Cs against pressure has a point of inflection which could not be predicted from the behavior at lower pressures; if other metals behave similarly above the present experimental range, it is possible that the resistance of all metals will eventually pass through a minimum. Such a change for Rb may be expected below 20000 kg/cm². This reversal of resistance may be an indication of the first beginning of a quantum break-down, suggested more strongly by the volume relations. The discontinuity of resistance at melting is approximately constant for all the alkalies. (4) *Volume.* Cs is the most compressible solid element yet measured directly. Instead of the atom the electron seems to be the significant unit of structure for volume since the volume per electron and the compressibility per electron do not vary greatly throughout the alkali series, whereas atomic volume and atomic compressibility vary greatly. At atmospheric pressure the electronic volume of K is abnormal, standing between that of Li and Na, but at high pressures there is a reversal. At high pressures the electronic compressibilities of all the alkalies are roughly equal (2.2 to 3.5×10^{-29} at 12000 kg/cm²), except for K, which is twice as compressible per electron (5.9×10^{-29}). The initial high relative compressibilities of Cs and Rb decrease rapidly with pressure, crossing that for K below 8000 kg/cm², while the high compressibility of K persists over a wide pressure range with comparatively small drop. All the evidence indicates an abnormally open electronic structure for K. (5) *Comparison with compressibility of electron gas.* Numeri-

cally the compressibility of all the alkalies is of the order of magnitude of that of a perfect gas under a high internal pressure, taking the electron as the gas unit. For K, the compressibility has passed a turning point within the experimental range, and appears to be ultimately headed for the perfect gas value. This may be the beginning of the quantum break-down, which is complete only at remotely high pressures. On the theoretical side, Schottky's theorem, in conjunction with the extrapolated behavior of compressibility, indicates the same break-down at high pressures.

Introduction

IN a paper now being published by the American Academy, data are given for several of the properties of rubidium and caesium under high pressure. Similar data have been previously published for Li, Na, and K,[1] so that the materials are now at hand for a systematic study of the effect of pressure on the properties of all the alkali metals. The data include the pressure-volume relations, and the effect of pressure on melting and electrical resistance. It is the purpose of this paper briefly to summarize the new data, and then to make a comparative study of the behavior of the five metals under pressure. Such a study may be expected to be of special significance because the effects of pressure on these metals are unusually large; Cs, for example, is by far the most compressible element solid under usual conditions, and is even more compressible over a wide range of pressure than the most compressible organic liquids, such as ether. From a study of these metals, if at all, we may expect light on the question of the ultimate behavior as pressure is increased indefinitely. Recent astronomical speculations deal with densities of 50000; such densities can exist only when the quantum structure of the atoms has entirely broken down and matter is resolved into a gas of electrons and nuclei. Some such break-down of the quantum orbits must of course take place at ordinary temperatures if the pressure is high enough; one of the questions that we shall consider here is whether the high pressure behavior of these metals suggests at all the beginning of such an atomic disintegration.

The New Data

Melting. The melting data for Rb and Cs are summarized in Table I. In broad features the behavior is the same as that found for all other substances under pressure; the curve of melting temperature against pressure is concave toward the pressure axis, the curve of the change in volume on melting, ΔV, against pressure is convex toward the pressure axis, and the latent heat is comparatively constant. The increase of the

[1] P. W. Bridgman, Phys. Rev. **3**, 154-157 (1914); **6**, 31 and 102 (1915); Amer. Acad. Proc. **56**, 67, 76, and 82 (1921).

latent heat of Cs under pressure is rather greater than usual. These new data on the most compressible metals give no reason to alter the conclusion previously drawn as to the character of the melting curve, namely that the melting curve probably rises indefinitely with continually decreasing curvature, but with neither maximum nor critical point.

TABLE I

Melting data for rubidium and caesium

Pressure (kg/cm²)	Rubidium Temp.	Rubidium ΔV (cm³/gm)	Rubidium Latent heat (kg · m/gm)	Caesium Temp.	Caesium ΔV (cm³/gm)	Caesium Latent heat (kg · m/gm)
1	38°.7	.0185	2.76	29°.7	.0136	1.65
500	48 .7	163	2.73	41 .4	118	1.68
1000	57 .9	145	2.70	51 .9	105	1.72
1500	66 .5	130	2.66	61 .4	96	1.76
2000	74 .5	119	2.67	70 .2	88	1.80
2500	82 .0	112	2.72	78 .3	83	1.88
3000	89 .1	106	2.76	85 .7	78	1.99
3500	95 .9	101	2.78	92 .4	75	2.14
4000				98 .5	72	2.29

A word should be said about the character of the melting. The melting points found for these metals are materially higher than those usually listed in the literature and the melting was very sharp, both evidence of high purity. It is more than usually difficult to obtain these metals pure; the impurity difficult to remove is not another metal, but oxide, which dissolves in the metal like a foreign metal and depresses the freezing point. Purification demands long slow distillation in high vacuum at the lowest possible temperature. The criterion of sharp freezing is one of the most delicate for high purity, and results should not be accepted for these metals unless the freezing is sharp. Thus the results recently published by Bidwell[2] on the thermo-electric properties of Rb and Cs, which he interprets as due to some sort of internal change in the metals, I believe are much more likely to be due to dissolved impurity. Bidwell's metals left much to be desired as to sharpness of freezing.

Electrical resistance. The data on electrical resistance are too numerous to summarize here, but the most important results, those for the solid metals, are summarized in Table II. It is to be emphasized that the resistance measurements on the solid were made on bare wires; internal stresses introduce too large errors if the metal is enclosed in a glass capillary as has usually been done. In addition to the data of Table II, the detailed paper gives the resistance of the liquid under pressure,

[2] C. C. Bidwell, Phys. Rev. **23**, 357-376 (1924).

the temperature coefficients at atmospheric pressure, a study of the effect of pressure on the temperature coefficient of the solid, and the change with pressure of the discontinuity of resistance on melting.

By far the most important of the new results is the establishment of the minimum resistance of solid Cs. Initially, at atmospheric pressure, the resistance of Cs decreases more rapidly than does that of any other metal, but the rate of decrease rapidly diminishes, until near 4000 kg/cm² there is a flat minimum, and from here on the resistance increases smoothly. This is the only example of a minimum yet found.

TABLE II

Electrical resistance data for Rb and Cs

Pressure (kg/cm²)	Relative resistance of solid bare wire to values for 1 kg/cm², at 0°C		
	Rubidium		Caesium
	0°	35°	0°
1	1.000	1.205	1.000
1000	.845	.982	.863
2000	.733	.840	.779
3000	.648	.740	.729
4000	.583	.663	.709
5000	.531	.602	.713
6000	.490	.553	.728
7000	.456	.514	.756
8000	.428	.481	.794
9000	.406	.455	.833
10000	.387	.434	.879
11000	.372	.418	.931
12000	.360	.406	.994

In a previous paper I made a preliminary announcement that Cs has a second polymorphic modification at high pressures, and that the resistance of this modification increases with pressure. This was an error; the apparent discontinuity which I ascribed to a polymorphic modification turns out to be connected in some way with the separation of impurity and disappears entirely when the purity is sufficiently increased, so that we are left with the perfectly smooth passage of the resistance through a minimum.

The discontinuity of resistance between solid and liquid is approximately constant along the melting curve, decreasing slightly with rising pressure for Rb, and increasing slightly for Cs. The same approximate constancy of the ratio of resistance of solid to liquid has been found for other metals. The temperature coefficient of resistance of solid Rb decreases from 0.00481 at 1 kg/cm² to 0.00365 at 11000, but for solid Cs the temperature coefficient decreases from 0.00496 at 1 kg/cm² to 0.00366 at 6000, and then increases again to 0.00418 at 12000. This is the first example found of a temperature coefficient increasing with rising pres-

sure; it is doubtless connected in some way with the minimum of resistance.

With the improved technique now available, results found previously for K were re-examined. Measurements on the temperature coefficient of K in glass had previously shown a very marked decrease beyond 6000 kg/cm²,[3] a decrease shown by no other metal. The measurements were now repeated with bare wire, with the results that very little decrease was found beyond 6000, a result agreeing with that for all other metals. Doubtless the former results were due to the constraints exerted by the walls of the glass capillary.

Pressure-volume relations. The pressure-volume relations are summarized in Table III. The pressure range is here 15000 kg/cm² against the 12000 of my other work. The greater range was probably responsible for a somewhat lower accuracy, particularly at the upper end of the

TABLE III

Relative volumes for Rb and Cs
(Referred to values for 1 kg/cm²)

Pressure (kg/cm²)	Rubidium 50°C	Caesium 50°C
1	1.000	1.000
1000	.953	.941
2000	.914	.898
3000	.883	.866
4000	.857	.839
5000	.836	.816
6000	.819	.796
7000	.803	.777
8000	.789	.760
9000	.777	.745
10000	.766	.731
11000	.756	.718
12000	.746	.706
13000	.737	.694
14000	.729	.683
15000	.721	.672

range. In the detailed paper will also be found a few values for the volume of the liquid phase and also rough measurements of the thermal expansion. The data show that Cs is the most compressible of the solid elements directly measured (indirect inference, however, shows that at least solid hydrogen and helium are much more compressible,[4] but direct observations on these will not be feasible for a long time). At 12000 kg/cm² the volume of Cs has been reduced by very nearly the same amount as that of ether, but there is an essential difference in that the

[3] P. W. Bridgman, Amer. Acad. Proc. **56**, 140 (1921).
[4] P. W. Bridgman, Amer. Acad. Proc. **59**, 198 (1924).

compressibility of Cs is less affected by pressure than is that of ether. The initial compressibility of Cs is less than that of ether and its compressibility at 12000 greater, so that at higher pressures (20000 kg/cm², for example) the volume of Cs will be very materially less than that of ether.

Comparative Discussion

Melting data. In Fig. 1 are plotted in one diagram the melting points of the five alkali metals as a function of pressure. The most interesting

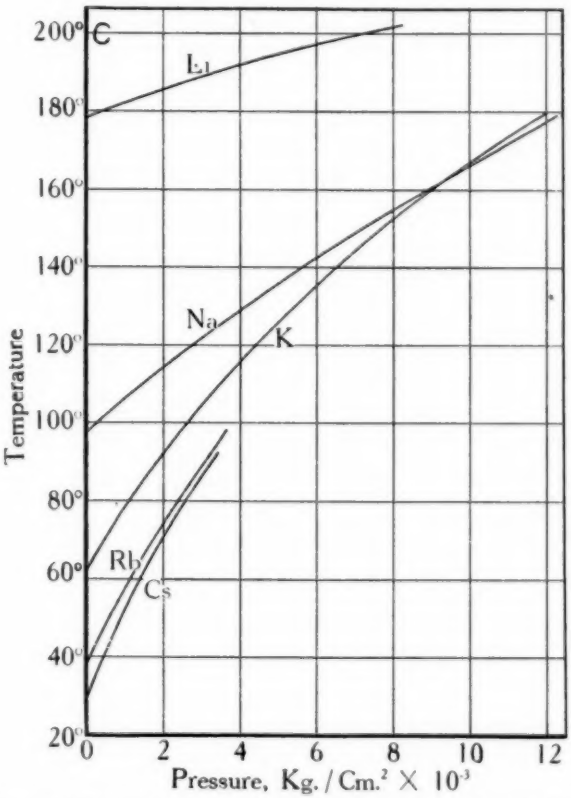

Fig. 1. The melting temperatures of the alkali metals as a function of pressure.

feature is the crossing of the curves for Na and K, so that above 10000 kg/cm² the melting point of K is higher than that of Na, reversing the normal order. The diagram suggests strongly that there are other crossings at higher pressures; it seems almost certain that K will cross Li, and highly probable that Na will also cross Li. It is more difficult to estimate the future course of the curves for Rb and Cs, because these are given over only a small range, but it is not at all improbable that

these two curves will eventually cross all the others, so that at sufficiently high pressures the order of melting may be Cs, Rb, K, Na, and Li, the reverse of the usual order. This is not at all an unnatural state of affairs. At high pressures we may expect the atoms to become so packed in together that they find difficulty in melting; this packing effect will increase with the complexity of the atom, and the most complicated atom, Cs, will have the highest melting point.

The pressure at which this reversal of the ordinary melting points will be accomplished may be estimated by graphical extrapolation to be of the order of 25000 kg/cm². Such a pressure is comparatively low, much too low to produce those ultimate effects to be expected at extreme pressures when the quantum orbits break up. Under such pressures it will be shown that the volume relations of K differ from those of the other metals; it might be thought that the crossing of the melting curves is similarly an effect due to the unique behavior of K. This, however, I do not believe to be the case; the shape of the melting curves themselves, and also the fact that if melting temperature at atmospheric pressure is plotted against atomic number, K will be found to lie smoothly with the other metals, both suggest that K is not unusual with regard to melting. The peculiar volume relations of K to be discussed later do not seem strongly to affect the melting behavior.

The other melting data relating to change of volume and latent heat are also significant. It is evident that melting is an atomic phenomenon, and the five alkali metals should be compared on an atom for atom basis. Table IV shows the latent heat of melting at atmospheric pressure per gm atom. On passing from the solid to the liquid state approximately the same heat is absorbed per atom by all the alkalies (except Li). Under high pressure the latent heats vary in a complicated way, but not by large amounts, so that over the entire pressure range the generalization holds that the latent heat of melting per atom is approximately the same.

TABLE IV

Melting data at atmospheric pressure

Metal	Latent heat (kg · m/gm · atom)	Fractional change of volume
Li	49	.0060
K	215	.0231
Cs	219	.0256
Rb	236	.0284
Na	271	.0271

Table IV shows also that, except for Li, the fractional change of volume on melting is approximately the same, that is, on passing from

the solid to the liquid state an atom of an alkali metal experiences a definite fractional increase of volume.

Lithium is unique in its melting phenomena. The reason doubtless is to be sought in the structure of the atom; the number of electrons is so small, only three, that the external symmetry of the atom must be much lower than that of the other four alkalies.

Electrical resistance. Unlike many of the other properties, the electrical resistance of the alkali metals does not vary smoothly in the same direction throughout the series. Thus the specific resistance at 0°C at atmospheric pressure decreases from Li to Na, and then increases again from K to Rb to Cs. The numerical values of the specific resistance are respectively 8.6×10^{-6}, 4.3, 6.1, 11.6, and 19. A somewhat more satisfactory basis for comparison is the "conductivity per atom," which is obtained by dividing the specific conductivity at a temperature one half the characteristic temperature by $N^{1/3}$, where N is the number of atoms per cc. This is discussed more in detail in my forthcoming Solvay Conference report. If "conductivity per atom" is plotted against atomic number, a comparatively smooth curve will be found with a very pronounced maximum between K and Rb. A similar reversal within the series is shown by the pressure effects. In Fig. 2 the relative resistance at 0° is plotted against pressure. It is evident that there is some sort of a turning point between K and Rb.

The resistance of most metals decreases with rising pressure, but there are seven metals whose resistance increases. Among some 50 metals studied, the series of the alkali metals includes the numerical extremes of maximum positive and maximum negative pressure coefficients of resistance.

It is of interest that the abnormal pressure effects of both Li and Cs do not seem to be associated with the crystal structure of the solid but are more intimately connected with the atoms themselves. This is shown by the fact that the resistance of Li increases under pressure in the liquid as well as in the solid state. A corresponding experiment could not be made on the resistance of liquid Cs because within the temperature range of these experiments the liquid freezes at a pressure below that of the minimum resistance. But at 97° the freezing pressure is very close to that of the minimum resistance. The resistance of solid and liquid at this temperature was plotted in one diagram as a function of pressure, multiplying the resistance of the solid by such a factor as to remove the discontinuity at the freezing point. In this way a curve was obtained passing perfectly smoothly through the melting point. The obvious inference is that the crystal structure of the solid has nothing

to do with the minimum, and that at higher temperatures the resistance of the liquid as well will show a minimum.

A question of great importance for theories of resistance is whether the minimum resistance shown by Cs, the most compressible of the metals, will be shown by the other metals also at pressures high enough. This question can be answered only by some sort of extrapolation. Such an extrapolation is not easy from the curves of resistance given in

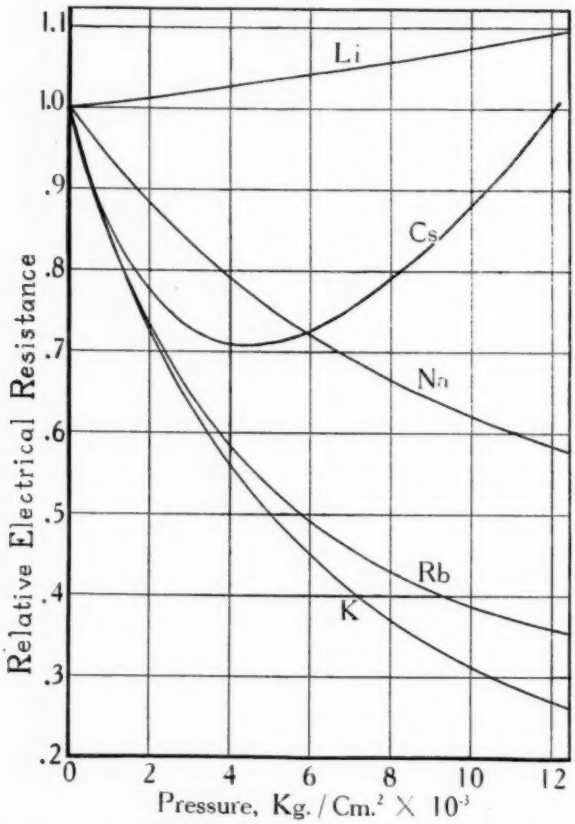

Fig. 2. The relative electrical resistances at 0°C of the alkali metals as a function of pressure.

Fig. 2. If, however, we plot $(1/w)(\partial w/\partial p)_T$ as a function of pressure, where w is resistance, we get something more suggestive as to the behavior at high pressure. For Cs, this quantity starts negative and crosses the axis at the pressure of the minimum, which is about 4400 kg/cm². The curvature against pressure is convex upward at pressures below 8000 kg/cm², but here there is a point of inflection, and above 8000, $(1/w)(\partial w/\partial p)_T$ increases at an accelerated rate with increasing

pressure. If this inflection is characteristic of the behavior of other metals at still higher pressures, then the resistance of each of them must also ultimately pass through a minimum. The shape of the curve for Rb indicates that this may well occur at some pressure below 20000 kg/cm^2.

We next have to ask what is the theoretical significance of this minimum resistance. The theory of electrical resistance which I have developed[5] represents the conduction electrons as passing through the substance of the atoms and encountering resistance where they make the jump from atom to atom. A minimum resistance is to be thought of as due to the fact that as the pressure is increased a point is reached beyond which the electrons find it increasingly difficult either to make the jump from one atom to the next or to get through the atom. Such interference with the electron is not surprising in a complicated structure distorted at high pressure. The minimum resistance is perhaps in Cs to be regarded as the first shadowing forth of the ultimate disintegration of the quantum orbits under extreme pressure. It is significant that the effect is first found in the most compressible metal with a complicated atomic structure.

Volume relations. In discussing melting phenomena we have seen that the atom is the significant unit of structure, as is shown for example by the fact that the latent heat of melting per atom is nearly the same for the four heavy alkalies. This is as we would expect, since the atoms pass as a unit from the liquid to the solid phase. But now that we are to discuss volume relations, it will appear that the electron, the ultimate constituent of the atom, is the more significant unit of structure; this is suggested by the fact that the contributions made to the volume or to the compressibility per electron vary much less from one alkali to another than do the contributions per atom.

We first compare the volume per electron in the five metals as a function of pressure. The volume per electron is obtained from the volume per atom by dividing by the atomic number plus 1 (that is, we are obtaining the average volume occupied by one discrete piece of electricity, whether positive or negative, the nucleus counting as one). The volume per atom is the atomic weight multiplied by 1.66×10^{-24} (the weight of the atom of hydrogen) divided by the density. Thus we find, for example, the volume per electron of Li at atmospheric pressure is $6.94\times1.66\times10^{-24}/4\times.53=5.43\times10^{-24}$ cm^3.

[5] P. W. Bridgman, Phys. Rev. **19,** 269-289 (1917); **17,** 161-194 (1921); **19,** 114-134 (1922); Report of the Solvay Conference, Brussels, 1924 (not yet published).

In Fig. 3 is plotted the volume per electron as a function of pressure. Li has the largest and Cs the smallest electronic volume, that is, the quantum orbits are closely packed in Cs but loosely packed in Li. The electronic volume of Li at atmospheric pressure is 2.6 fold greater than that of Cs. On the other hand, if we compared atomic volumes, we would find the volume of Li to be least, and that of Cs greatest, 5.3 times that of Li. The variability of volume throughout the series of the alkalies is thus twice as great when expressed in terms of the atom as when expressed in terms of the electron.

At atmospheric pressure the electronic volume of K is greater than that of Na, a reversal of order. At high pressures, however, the curves

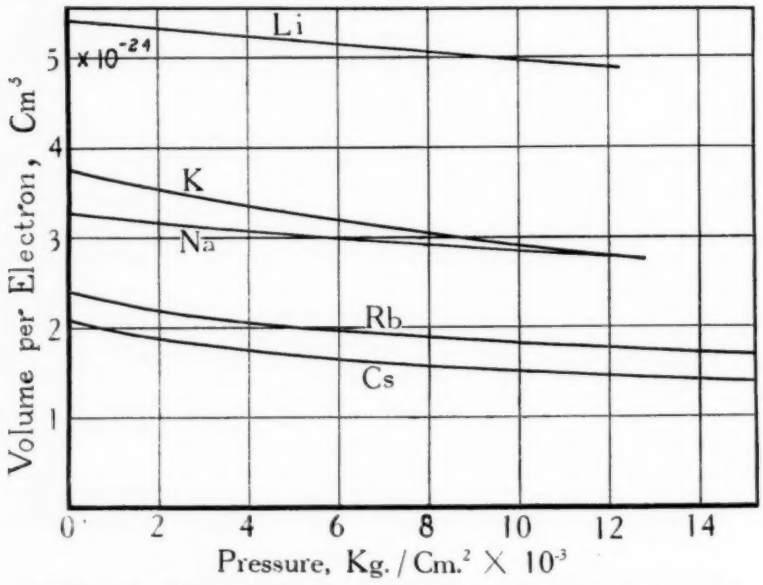

Fig. 3. The volume per electron in cm³ of the alkali metals as a function of pressure.

for K and Na cross. This is the first of several pieces of evidence that the electronic structure of K is abnormally loose.

It is evident from Fig. 3 that the shapes of the curves of electronic volume against pressure are distinctly different for the different alkalies. This difference is brought out much more strikingly in Fig. 4 in which is plotted the instantaneous compressibility, $(1/v)(\partial v/\partial p)_T$, as a function of pressure. If the curves of volume against pressure were of the same shape, the curves of $(1/v)(\partial v/\partial p)_T$ against pressure would be the same for all the metals. This is evidently far from being the case. Not only are the absolute values of $(1/v)(\partial v/\partial p)_T$ quite different, but

the shapes of the curves are very different. This has a bearing on speculations of Richards[6] as to the internal pressures of the alkalies. In endeavoring to find some rational basis for extrapolation, he made the assumption that the pressure-volume curve at low pressures of a comparatively incompressible alkali was of the same shape as the pressure-volume curve at high pressure of a more compressible alkali; that is, if all the ordinates of the pressure-volume curve of one metal were

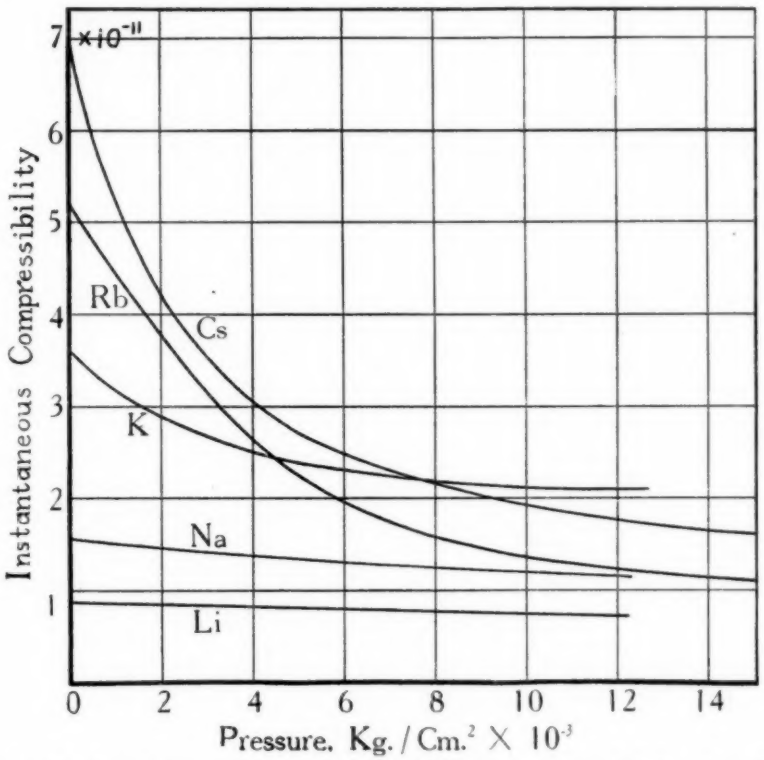

Fig. 4. The instantaneous compressibility $(1/v)(\partial v/\partial p)_T$ in Abs. C.G.S. units, of the alkali metals as a function of pressure.

multiplied by an appropriate constant and then the curve slid bodily along the pressure axis, the curve so found would coincide with the prolongation into a region as yet unreached experimentally of the pressure-volume curve of another alkali. In particular, he applied this method of extrapolation to Na and K. At the time that he did this, these data for Cs and Rb were not available. These new data show definitely that the assumed connection between the different metals

[6] T. W. Richards, Jour. Amer. Chem. Soc. **45**, 422-437 (1923).

does not exist, for if it did, the curves could not cross in the way they do. Richard's method of extrapolation can therefore be regarded as only roughly suggesting what to expect at high pressure; it is probable, however, that the approximation was sufficiently good for the purpose for which Richards used it.

The most striking feature of Fig. 4 is the crossing of the curves for Cs and Rb by that of K; this means that K retains its compressibility to an abnormal degree at high pressures. This again points to a looseness of internal structure. Another striking feature is the great progressive change in the character of the curves throughout the series. In 12000 kg/cm² the compressibility of Li drops to 0.83 of its initial value, whereas that of Cs drops to 0.23. The rapid drop of compressibility with increasing pressure is partly due, especially for the more compressible metals, to a taking out of "slack" from the structure by pressure. In the most complicated structure, that of Cs, the possibility of taking out slack is most rapidly exhausted, giving the most rapid drop of compressibility with increasing pressure.

The extent to which the "slack" in the structure is responsible for the initial behavior is further indicated by Table V which shows the compressibility per electron, that is, the actual loss in volume per electron under a pressure increase of 1 kg/cm², at 1 and 12000 kg/cm², for the 5 metals. Under 12000 the approximate constancy of the compressibility per electron for all the metals (except K) is striking, especially when compared with the initial variability. Li has the greatest compressibility per electron at high pressure, as we would expect because of

TABLE V

Volume compression per electron per kg/cm²

Metal	Electronic compression	
	Atms. pressure	12000 kg/cm²
Li	4.7×10^{-29}	3.5×10^{-29}
Na	5.1	3.2
K	13.5	5.9
Rb	12.5	2.2
Cs	14.5	2.5

its more open structure. However, the difference is not as great as might be expected. At 12000 the electrons are packed 3.3 times more loosely in Li than in Cs, but the compressibility is only 1.4 times greater. K is an outstanding exception, both in its initial compressibility (too great to lie in a smooth series with the others) and in its persistent compressibility at high pressures, about twice as high as the average of the others.

Finally we have to consider whether there is any indication within the pressure range reached experimentally of the beginning of the breakdown of the quantum structure which we may expect must be inevitable if the pressure can only be pushed high enough. An inquiry of this sort must, of course, be highly speculative. We take as our clue the recent speculations of astronomers that in the interiors of the stars matter may be disintegrated into a gas of electrons and nuclei.

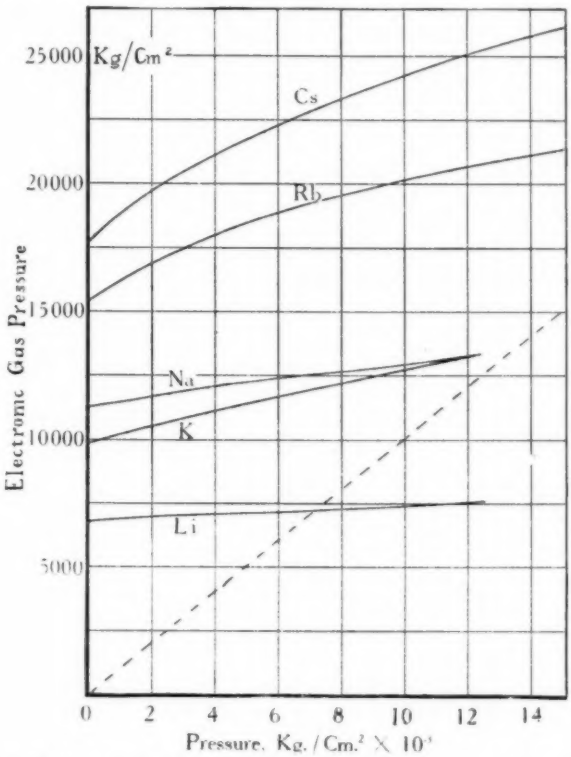

Fig. 5. The electronic gas pressures (that is, the pressures which would be exerted by the electrons and nuclei if they were in the condition of a perfect gas under the actual volume of the metal) of the alkali metals at 0°C as a function of external pressure.

It is in the first place to be noticed that the pressures which would be exerted by these alkali metals if electrons and nuclei constituted a perfect gas are not excessively high. The material for such a calculation is already at hand; we have merely to divide the reciprocal of volume per electron (number of electrons per cm^3) by 2.7×10^{19}, the number of gas molecules per cm^3 at 0°C at 1 atmosphere. In this way the curves of Fig. 5 were obtained. The pressures are of the order of tens of thousands of kilograms per cm^2, which is the order of experi-

mentally obtainable pressures. It is therefore not extravagant to think that experimentally obtainable pressures may at least initiate the reversion to the perfect gas condition. The direction in which the quantum forces act is shown in the figure by the location of the gas pressure curve with respect to the 45° line. The curve for Li crosses this line at 7000; above 7000 the electrons in the perfect gas state would not be able to withstand the external pressure, so that if the quantum forces were removed the structure would collapse. Hence above 7000 the quantum forces distend the structure, whereas below 7000 they prevent it from flying apart. It is also evident from the figure that below 15000 kg the quantum forces in Na and K will change from an expansive to a compressive character. It seems probable that Rb and Cs will similarly change at considerably higher pressures.

When the structure breaks down completely into a perfect gas, the gas pressure curve will coincide with the 45° line, or at least will run parallel to it. The figure shows that any such state of affairs is remote, but there are two indications of the beginning of an approach to it. In the first place, it is evident that K comes nearest of the three lightest alkalies to satisfying this condition, because the slope of its gas pressure curve is closest to 45°. But if there is ever going to be coincidence or parallelism with the 45° line, it is evident that the gas pressure curve must be concave upwards, whereas at low pressures all the curves are concave downward, as is shown in the figure most unmistakably by the entire course of the curves of Rb and Cs. Now this necessary reversal of curvature is indeed shown, well beyond experimental error, both by K and Li, although the effect is not large enough to be well marked in the diagram, and probably is shown by Na also, although it is not so certain that experimental error may not enter here.

The effect is exhibited more clearly if we consider the compressibility instead of the volume. The question is whether the compressibility of the solid alkali metals has features in common with the compressibility of a perfect gas. The compressibility of a perfect gas is $(1/v)(\partial v/\partial p)_\tau = -1/p$. But when we attempt to apply this expression to our solid metals we encounter the difficulty of not knowing the internal pressure. We avoid this difficulty by eliminating p by dividing both sides of the equation by v_e, where v_e is the average volume occupied by one electron, using the gas law $pv_e = 1.35\times10^{-16}\tau$, and obtain:

$$\frac{1}{v_e}\left[\frac{1}{v}\left(\frac{\partial v}{\partial p}\right)_\tau\right] = \frac{-1}{1.35\times10^{-16}\tau} = -2.4\times10^{13} \text{ at } 300°\text{K}.$$

The material is at hand for a calculation of $(1/v_e)(1/v)(\partial v/\partial p)_\tau$, which we will call the "gas function," as a function of pressure. The results

are shown in Fig. 6. It is significant that the gas function is of the order of magnitude of -2.4×10^{13}, which is the value it would have if the solid were to act like a perfect gas under some unknown but high pressure and in which the *kinetic unit is the individual electron.* If we assumed that the atom were the unit, the gas function would be of a different order of magnitude. The approach of the gas function to the value of a perfect gas is closest for Cs and most remote for Li. In speculating now as to the behavior at very high pressures, the shape of the curve for the gas function is significant. The curves for Cs and Rb are

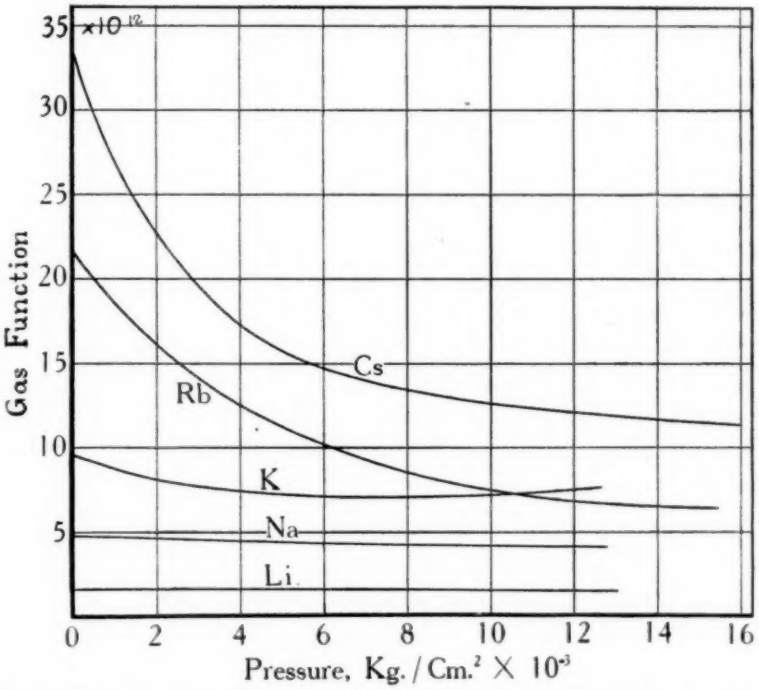

Fig. 6. The "gas function" $(1/v)(1/v)(\partial v/\partial p)_T$ of the alkali metals as a function of external pressure. If the metals acted like a perfect gas of electrons and nuclei, the gas function would have the constant value 24×10^{12}.

still receding from the perfect gas value at the highest pressures reached experimentally, whereas for K a reversal has been reached at 7000 or 8000 kg/cm², and above this pressure the gas function of K has started to approach more closely to the value for a perfect gas. It is tempting to see in this the beginning of the quantum breakdown.

Apart from this experimental evidence, we may obtain some theoretical light on the question of the ultimate behavior under exceedingly

high pressures from a theorem due to Schottky.[7] He finds for any system in which there are forces between the elements given by the ordinary inverse square laws of electromagnetism and in which the elements move under these forces as if they had mechanical mass, whether or not the motion is in addition subjected to quantum forces, the following equations:

$$\left(\frac{\partial \bar{L}}{\partial p}\right)_\tau = 3v + \tau\left(\frac{\partial v}{\partial \tau}\right)_p + 4p\left(\frac{\partial v}{\partial p}\right)$$

$$\left(\frac{\partial \bar{E}}{\partial p}\right)_\tau = -3v - 2\tau\left(\frac{\partial v}{\partial \tau}\right)_p - 5p\left(\frac{\partial v}{\partial p}\right)_\tau ,$$

where $\bar{L}$ is the average internal kinetic energy of motion of the elements, and $\bar{E}$ is the average electromagnetic potential energy. The total internal energy $\bar{U}$ of the system is of course given by $\bar{U} = E + \bar{L}$. The equations in the form above were not given by Schottky, but may be deduced from equations given by him by using the ordinary thermodynamic relation

$$\left(\frac{\partial \bar{U}}{\partial p}\right)_\tau = -\tau\left(\frac{\partial v}{\partial \tau}\right)_p - p\left(\frac{\partial v}{\partial p}\right)_\tau .$$

At 0°K we have rigorously

$$\left(\frac{\partial \bar{L}}{\partial p}\right)_\tau = 3v + 4p\left(\frac{\partial v}{\partial p}\right)_\tau$$

$$\left(\frac{\partial \bar{E}}{\partial p}\right)_\tau = -3v - 5p\left(\frac{\partial v}{\partial p}\right)_\tau .$$

These relations are also approximately true at other temperatures, for on substituting numerical values for ordinary solid metals it appears that the term $\tau(\partial v/\partial \tau)_p$ is unimportant. Now in the equations as last given the term v is positive and $p(\partial v/\partial p)_\tau$ is negative. At zero pressure only the term v contributes, and $\bar{L}$ increases with increasing pressure and $\bar{E}$ diminishes. But with increasing pressure v diminishes and $p(\partial v/\partial p)_\tau$ increases. Will the second term eventually become larger than the first? We attempt to answer this by plotting $-(p/v)(\partial v/\partial p)_\tau$ against pressure for the five alkali metals. Fig. 7 shows the result. If $-(p/v)(\partial v/\partial p)_\tau$ becomes equal to 0.6, the direction of variation of $\bar{E}$ changes, and if it reaches 0.75, the direction of variation of $\bar{L}$ changes.

[7] W. Schottky, Phys. Zeits. **21**, 232 (1920).

Again K is the most suggestive metal. For it, $(p/v)(\partial v/\partial p)_\tau$ is nearly linear against pressure; as a matter of fact at low pressures the curve is slightly concave toward the pressure axis, but at high pressures it becomes slightly convex. $(p/v)(\partial v/\partial p)_\tau$ therefore rises at an accelerated rate as pressure increases, and the critical value 0.6 will be reached at a pressure near 30000 kg. The curves for the other metals are also flattening out at a rapid rate, so that is it probable that for all the alkalies the critical value will be eventually exceeded.

What now is the significance of the change of L and E? Initially the state of affairs is plain. In general an increase of L means an increase of rapidity of motion of the electrons in their orbits, which means an

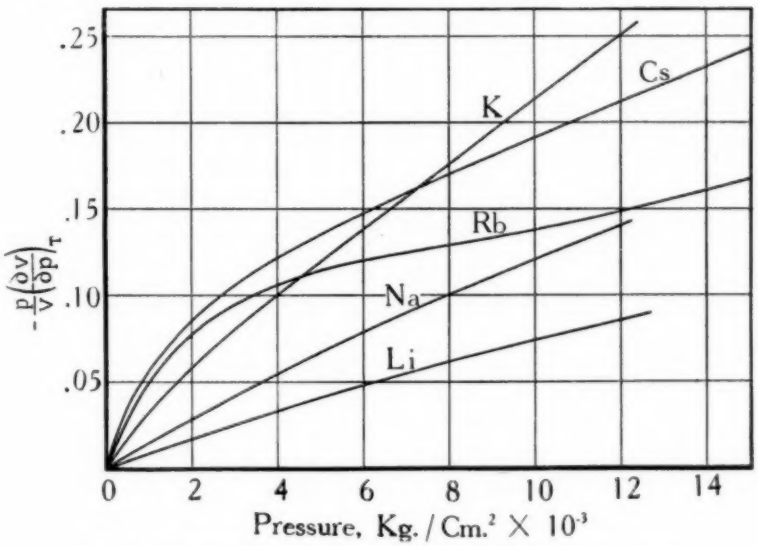

Fig. 7. The function $-(p/v)(\partial v/\partial p)_\tau$ of the alkali metals as a function of external pressure.

approach on the average to the attracting nuclei. The same approach to the nuclei which increases L brings the electrons into stronger parts of the fields of the nuclei and thus at the same time provides for the decrease of E. This approach to the nuclei may be thought of as signifying a compression of the atoms under pressure, as Schottky suggested, or it may be thought of as follows. As we proceed through the series of the chemical elements from simpler to more complex, it is well recognized that the electron orbits penetrate more and more deeply toward the nucleus, and at the same time become more eccentric. The same sort of thing may very naturally be produced also when we push the electron orbits into closer juxtaposition by increasing pressure, so

that the initial increase of L and decrease of E with increasing pressure is accounted for by a deeper penetration of the orbits toward the nuclei. But now at higher pressures, how are we to account for a decrease of L and an increase of E, if according to our argument this means orbits described at greater distances from the nuclei? The difficulty is overcome if the electron orbits break down, allowing an approach to a more uniform distribution in space of electrons and nuclei. The electrons now do not penetrate so closely to the attracting nuclei, so that on the average L is smaller and at the same time E increases, both in spite of a continued decrease of total volume. But this sort of break-down means an approach to the condition of a gas. It thus appears that the dilemma to which Schottky's theorem, in conjunction with the experimental behavior of the compressibility of the alkali metals, forces us, is resolved by a break-down of the quantum orbits at sufficiently high pressures, and an approach to the condition of a gas.

JEFFERSON PHYSICAL LABORATORY,
HARVARD UNIVERSITY,
October 4, 1925.

BATEMAN'S EXTENDED ELECTRODYNAMICS, AND THE MASS AND RADIATION REACTION OF AN ELECTRON

By Meyer Salkover

Abstract

From Bateman's earlier stress-energy tensor, there are deduced by analogy with the momentum and energy equations based on the classical electromagnetic stress-energy tensor, an extra-classical body-force and a condition that may be understood to state the conservation of charge in combination with the Lorentz transformation. It is then shown how this procedure may be reversed so as to derive, from the new body-force and the condition just mentioned, Bateman's tensor with all of its components physically interpreted. Next the mass and radiation reaction of an electron in non-uniformly accelerated, non-periodic motion are calculated from the force (classical and extra-classical) exerted on it by its own field, on the assumptions that the electron is spherical in a rest-system and has a centrally symmetrical distribution of charge. Both come out zero. The result for the radiation reaction is new. Finally the same result for the mass is obtained from the total momentum of the field of an electron in uniform, or quasi-stationary, motion. The present method differs from one recently published by Bateman in not using the restricted relativity transformation for tensors, and in requiring of the distribution of charge only that it be centrally symmetrical.

Introduction

TO the stress-energy tensor T^e of classical electrodynamics, comprising the stress-system X_x^e, X_y^e. . . Z_z^e, the energy-flux (Poynting's) vector $\mathbf{S}^e$ and related density of momentum $\mathbf{G}^e$ and the energy-density W^e as deducible from the equations of Maxwell and Lorentz, Bateman has successively added new tensors[1] designed to remedy defects of the classical theory. The fundamental one of these tensors, and the only one that will be considered here, is T^s, having as components

$$X_x^s = -2\psi\frac{\partial^2\psi}{\partial x^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

$$X_y^s = Y_x^s = -2\psi\frac{\partial^2\psi}{\partial x\partial y}$$

$$W^s = 2\psi\frac{\partial^2\psi}{\partial t^2} + \left(\frac{\partial\psi}{\partial x}\right)^2 + \left(\frac{\partial\psi}{\partial y}\right)^2 + \left(\frac{\partial\psi}{\partial z}\right)^2 - \frac{1}{c^2}\left(\frac{\partial\psi}{\partial t}\right)^2$$

$$S_x^s = c^2 G_x^s = -2\psi\frac{\partial^2\psi}{\partial x\partial t}$$

[1] H. Bateman, Phys. Rev. **20**, 243 (1922); Bull. Nat. Res. Council, **24**, p. 99 (1922); Messenger of Mathematics **52**, 116 (1922); Ibid. **53**, 145 (1924); Phil. Mag. **49**, 1 (1925).

where ψ is a retarded scalar potential defined by

$$\psi = \int \left[\rho\sqrt{1-(v^2/c^2)}\,\right]_{t-r/c}(dV/r)$$

and consequently satisfying the differential equation

$$\frac{\partial^2\psi}{\partial x^2}+\frac{\partial^2\psi}{\partial y^2}+\frac{\partial^2\psi}{\partial z^2}-\frac{1}{c^2}\frac{\partial^2\psi}{\partial t^2}=-\rho\sqrt{1-(v^2/c^2)}$$

Since the right side of this equation is an invariant with respect to the Lorentz transformation, as is also the differential operator on the left side, it follows that the potential ψ is such an invariant. The tensor T^s is then readily shown to be a symmetrical world-tensor[2] with the same transformational properties as T^e.

The components of the body-force associated with T^s are determined by relations of the type

$$F_x{}^s=\frac{\partial X_x{}^s}{\partial x}+\frac{\partial X_y{}^s}{\partial y}+\frac{\partial X_z{}^s}{\partial z}-\frac{\partial G_x{}^s}{\partial t} \tag{1}$$

which are identical in form with the relations between the classical body-force

$$\mathbf{F}^e=\rho\left(\mathbf{E}+\frac{1}{c}\mathbf{v}\times\mathbf{H}\right)$$

and the tensor T^e. The results may be combined in the vector equation

$$\mathbf{F}^s=2\psi\nabla\left\{\rho\sqrt{1-(v^2/c^2)}\,\right\}. \tag{2}$$

Corresponding to the classical energy-equation, we have also

$$\mathbf{v}\cdot\mathbf{F}^s+\mathrm{div}\mathbf{S}^s+\frac{\partial W^s}{\partial t}=0 \tag{3}$$

provided that

$$\psi\frac{d}{dt}\left\{\rho\sqrt{1-(v^2/c^2)}\,\right\}=0 \tag{4}$$

It is possible to proceed in another manner, following the usual treatment of classical electron theory. If we assume Eq. (2), then by an integration of $\mathbf{F}^s$ over all space and a reduction by means of Green's Theorem, the expressions previously labeled as $X_x{}^s$, $X_y{}^s$ . . . $Z_z{}^s$ and $\mathbf{G}^s$ are obtained and seen to have physical meanings consistent with the names assigned to them. Details will not be given; the process, though rather lengthy, is direct, and offers no essential difficulties. Eq. (1) follows as a corollary. In the same way, starting with an integration of the

[2] M. v. Laue, Die Relativitätstheorie, 4. Aufl., 1. Bd., p. 102.

activity of the body-force, $\mathbf{F}' \cdot \mathbf{v}$, we can derive the rest of the tensor T' and Eq. (3), if

$$\frac{d}{dt}\{\rho\sqrt{1-(v^2/c^2)}\}=0\,.$$

The last assumption, which is not altogether the same as Eq. (4), may be granted, since it amounts to the conservation of charge as combined with the Lorentz transformation.

Mass and Radiation Reaction

The reaction on an electron of its own field will now be considered. The electron will be taken as spherical when at rest, with a volume charge distributed symmetrically about the center, but otherwise arbitrarily. The motion of the electron will be unspecified except for the supposition that there is always a reference system of the type dealt with in the restricted theory of relativity in which the electron is momentarily at rest, with acceleration and derivative of acceleration not varying from point to point, and that, relative to this system, the electron is spherical and has the stationary distribution of charge.

On these assumptions, the classical reaction, so far as it depends on the acceleration ($\mathbf{f}$) and derivative of the acceleration ($\dot{\mathbf{f}}$), is[3]

$$-(\mathbf{f}/6\pi c^2)\int \rho dV \int \rho' dV'(1/(R^2+R'^2-2RR'\cos\theta)^{1/2})+e^2\dot{\mathbf{f}}/6\pi c^3$$

where ρ and ρ' are the densities of charge at volume elements dV and dV' which lie, respectively, at distances R and R' from the center, along radii vectors enclosing the angle θ.

To get the extra-classical reaction, we start with Eq. (2). Here, to allow for the rest-system used, we put $v=0$. The part of ψ due to element of charge de at a field-point relative to which the position of de is given by the vector $\mathbf{r}$ is

$$de[\sqrt{1-(v^2/c^2)}\,]/4\pi[r(1+(\mathbf{r}\cdot\mathbf{v}/cr))]$$

where the bracketed quantities must be assigned the values pertaining to the previous time $t-[r]/c$. This expression, reduced by means of known series expansions[4] so as to involve only magnitudes evaluated at the time t becomes, as far as terms in $\dot{\mathbf{f}}$,

$$\frac{de}{4\pi}\left(\frac{1}{r}+\frac{1}{2}\,\frac{\mathbf{f}\cdot\mathbf{r}}{rc^2}-\frac{1}{3c^3}\dot{\mathbf{f}}\cdot\mathbf{r}\right)$$

[3] L. Page, Introduction to Electrodynamics, pp. 51 52.
[4] Ref. 3, pp. 39, 40.

Next, changing de to $\rho' dV'$, multiplying by $2\nabla\rho dV$, and integrating twice through the electron, we have, omitting the electrostatic term that contributes nothing,

$$\frac{\mathbf{f}}{4\pi c^2 f}\int dV \cos\alpha(\mathbf{f}\cdot\nabla\rho)\int\frac{\rho' dV'(R'\cos\theta - R)}{\sqrt{R^2+R'^2-2RR'\cos\theta}} + \frac{e\dot{\mathbf{f}}}{6\pi c^3}\int\cos^2\beta\frac{d\rho}{dR}dV$$

$$-\frac{\mathbf{f}}{4\pi c^2}\int_{R=a}\rho\cos^2\alpha dS\int\left[\frac{\rho' dV'(R'\cos\theta - R)}{\sqrt{R^2+R'^2-2RR'\cos\theta}}\right]_{R=a}$$

$$-\frac{e\dot{\mathbf{f}}}{6\pi c^3}\int a\rho_{R=a}\cos^2\beta dS$$

where α, β are the angles between $\mathbf{R}$, and $\mathbf{f}$ and $\dot{\mathbf{f}}$, respectively. The surface integrals arise from the infinite discontinuity of $\nabla\rho$ at the surface, $R=a$.

By the use of Gauss' Theorem, the surface integrals may each be proved equal to the negative of the sum of the corresponding classical and extra-classical volume reactions, so that for any centrally symmetrical distribution of charge (which may be very different from the distribution designed by Bateman to secure equilibrium within the stationary electron[5]) the $\mathbf{f}$ and $\dot{\mathbf{f}}$ reactions vanish.

The vanishing of the $\mathbf{f}$ reaction is interpreted to mean that the mass is zero, and this is in agreement with the result in the final section where the case of uniform (or quasi-stationary) motion is treated. By introducing (in the last three of his papers[1]) new tensors to remove certain surface discontinuities in the components of T^e+T^s for the stationary electron, Bateman succeeds in rendering the mass different from zero—the actual value obtained, regardless of the way in which density varies with distance from the center, is three times the mass of a Lorentz electron with a uniform surface distribution. But the $\dot{\mathbf{f}}$ reaction remains zero. This result seems to indicate that radiation is impossible. When, however, the

[5] This distribution is obtained by putting $F^e+F^s=0$ inside the stationary electron. The advantage it enjoys over other distributions is that, when additional tensors are introduced, it leads to the exact relativistic relation between energy of the stationary field and rest-mass; without the additional tensors, this energy is zero, as well as the rest-mass.

Bateman, however, repeatedly states that the resultant body-force should be postulated to vanish everywhere. While this is in the spirit of relativity mechanics, it may be pointed out that for the immediate purposes of his analysis such a generality is not essential. In one of his papers (Messenger of Mathematics **52,** 122 (1922)) Bateman appears to make elaborate use of it, but his results there can readily be derived without it.

energy radiated by a point charge is considered, it develops[1] that the energy radiation vanishes, on the average, only for periodic motion.[6]

Momentum of the Field for Uniform Motion

That the mass of an electron is zero may also be inferred from the vanishing of the total momentum of the field of an electron in uniform (or quasi-stationary) motion. Bateman[7] obtains this result by using a transformation formula applying to tensors in the restricted theory of relativity. The momentum in question is thus shown to be a multiple of the total energy of the field of a stationary electron with his equilibrium distribution of charge, and this he has found to be zero.

While the argument can be modified so as not to involve any particular distribution of charge, another deduction requiring only central symmetry and using simpler relativity transformations may easily be made as follows: As can be shown[8] by changing to the reference system in which the uniformly moving electron is at rest, the electromagnetic momentum of its field is

$$\frac{\mathbf{v}}{c^2\sqrt{1-(v^2/c^2)}}\int(\nabla\Phi)^2\sin^2\theta dV \tag{5}$$

where the integral is extended over all space. Φ is the electrostatic potential due to the electron; dV is in polar coordinates so that θ has its usual significance, the polar axis being the direction of motion (velocity = $\mathbf{v}$) in the original reference system. It remains to calculate the extra-classical momentum, whose effective density is

$$\mathbf{G}' = -\frac{2\mathbf{v}}{c^2 v}\psi\frac{\partial^2\psi}{\partial x\partial t}$$

if the electron moves along the x-axis. The integration will again be carried out in the rest-system. As may be inferred from the definition of ψ and its invariance with respect to the Lorentz transformation, or may otherwise be proved directly, on changing the reference system ψ becomes Φ. Applying the Lorentz transformation to the differential co-

[6] In his later papers, Bateman regards compensating negative energy radiation as a blemish in his theory. It is hard to gather from the context whether the tensor introduced in Messenger of Mathematics, **52,** 125 (1922) is meant to remove this blemish; if so, it does not serve its purpose, for calculation shows that it leaves the radiation of energy *in statu quo.*

[7] Messenger of Mathematics **53,** 147 (1924).

[8] L. Silberstein, Theory of Relativity, p. 214.

efficient and to the element of volume, we have for the extra-classical momentum

$$\frac{2\mathbf{v}}{c^2\sqrt{1-(v^2/c^2)}}\int \Phi \frac{\partial^2 \Phi}{\partial x^2} dV$$

or, by symmetry,

$$\frac{2\mathbf{v}}{3c^2\sqrt{1-(v^2/c^2)}}\int \Phi \nabla^2 \Phi dV \tag{6}$$

The trigonometric factor in the integrand of (5) may be replaced by 2/3. The sum of (5) and (6) is reducible to a surface integral by Green's Theorem, and this surface integral vanishes since Φ and $\nabla\Phi$ are finite and continuous at the surface of the electron and vanish at infinity.

The writer is greatly indebted to Professor Leigh Page of Yale University.

DEPARTMENT OF MATHEMATICS,
UNIVERSITY OF CINCINNATI,
September 14, 1925.

THE DISPERSION OF THE OPTICAL CONSTANTS OF MERCURY

By Brian O'Brien

Abstract

Measurements were made on clean mercury surfaces prepared by the method of Roentgen as used by Wheeler. The optical constants were determined *for the range* 4358 *to* 3022*A* using the method of Jamin. Light from a mercury arc was dispersed by a quartz spectroscope of the Littrow type with a fused silicon mirror to reduce scattered visible light, and a phosphorescent screen or fluorescent solution was used in making the readings. The results for *refractive index n, absorption coefficient nk* and computed percentage *reflectivity R* at normal incidence, are as follows:

	4358	4047	3650	3130	3022
n	0.88	0.79	0.64	0.44	0.55
nk	3.47	3.40	2.97	2.53	2.25
R	77	78	78	79	70

The beginning of a region of transparency is apparently indicated at 3022A.

Introduction

THE effects of slight surface films on values obtained for the optical constants of metals by katoptric methods was pointed out by Voigt.[1] To eliminate such films Drude[2] attempted to specify a so-called "normal" surface, but large inconsistencies still remained in his results even among successive measurements on the same reflecting surface. Minor,[3] Meier,[4] Tool,[5] Ingersoll,[6] and Tate[7] have measured the optical constants of several of the metals from wave-length 2500A (Minor) to wave-length 2.25μ (Ingersoll). The values obtained have been collected by Wheeler.[8] He has pointed out that while different observers are in good agreement as to the amount and trend of the dispersion of the refractive index and absorption coefficient of a particular metal over a given region, they are not in good agreement on the absolute magnitude of these constants.

Wheeler[9] has measured the refractive index of several transparent liquids in contact with mercury by the reflection method, using Roent-

[1] Voigt, Wied. Ann. **24,** Wied. Ann. **25,** (1885).
[2] Drude, Wied. Ann. **36,** 885; Wied. Ann. **39,** 481 (1899-1900).
[3] Minor, Ann. d. Physik **10,** 591 (1903).
[4] Meier, Ann. d. Physik **31,** 1017 (1910).
[5] Tool, Phys. Rev. **31,** 1 (1910).
[6] Ingersoll, Astrophys. J. **32,** 265 (1910).
[7] Tate, Phys. Rev. **33,** 321 (1912).
[8] Wheeler, Am. J. Sci. **35,** 491 (1913).
[9] Wheeler, Phil. Mag, **22,** 229 (1911); Am. J. Sci. **32,** 85 (1911).

gen's[10] modification of the method suggested by Rayleigh[11] to clean the surface of contact between the mercury and the transparent liquid. Differing from those of previous observers, his results are very consistent, and agree in the third place with values of the refractive index of the same liquids determined by the usual methods. It would appear therefore, that all contaminating films at the metal-liquid surface were eliminated. He has also measured the optical constants of mercury in air over a portion of the visible spectrum.[12]

The present investigation was undertaken to determine the optical constants of a mercury surface, cleaned in this manner, from the violet as far into the ultraviolet as feasible.

Method and Apparatus

The optical constants were determined by the usual method of measuring the ellipticity introduced into plane polarized light by reflection from the metal surface. The theory of the method has been given in detail by Drude.[2] If the incident light is plane polarized at an angle of 45° with the plane of incidence, if $\varphi \equiv$ the angle of incidence, $\Delta \equiv$ the phase difference after reflection between the components parallel and perpendicular to the plane of incidence, and $\psi \equiv$ the azimuth of the restored plane of polarization, then if we write

$$\tan Q \equiv \sin \Delta \tan 2\psi \; ; \qquad \cos P \equiv \cos \Delta \sin 2\psi \; ;$$

$$S \equiv \tan \tfrac{1}{2} P \sin \varphi \tan \varphi \; ;$$

we get to a second approximation

$$n = S \cos Q(1 + \sin^2\varphi / 2S^2)$$

$$nk = S \sin Q(1 - \sin^2\varphi / 2S^2)$$

$$k = \tan Q(1 - \sin^2\varphi / S^2)$$

where n is the refractive index and nk the absorption coefficient.

A spectrometer by the Société Genevôise, arranged so that the table could be swung to a vertical position to accommodate a horizontal mirror, was used as Jamin circle. The divided circle could be read to 20″ of arc. The polarizer and analyzer prisms were of the uncemented straight end type (Foucault-Glan), and their positions could be read to 0.1°. The compensator was of the Babinet-Soleil type, giving a uniform field instead of bands as in the original Babinet form. The movement of its

[10] Roentgen, Wied. Ann. **46,** 152 (1892).
[11] Rayleigh, Phil. Mag. (5) **30,** 392 (1890).
[12] O'Brien and Wheeler, Phys. Rev. (2) **21,** 376, Abs. 26 (1923).

wedge could be read to 0.0025 mm, which corresponded to an increment in Δ of 0.19° at the longest and 0.30° at the shortest wave-length used.

The source of light was a mercury arc in quartz, and a small quartz spectroscope of the Littrow type, which was built in this laboratory, was used as monochromatic illuminator. The reflector of the spectroscope was of fused silicon in place of the usual tin amalgam, the high ultraviolet and low visible reflectivity of the silicon reducing the effect of scattered visible light in the field.

The optical system is shown in Fig. 1. The mercury arc I was placed very close to the slit S_1 to eliminate a condensing lens. After passing through the analyzer the light was brought to a focus by the quartz lens L_3 on a fluorescent target F which was viewed from the side through an eyepiece E.

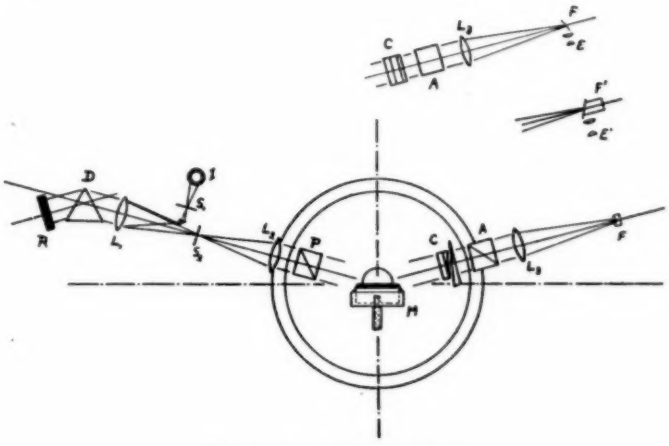

Fig. 1. The optical system.

A phosphorescent screen of very short period, and also a cell filled with a fluorescent solution were used. The screen consisted of varnished mica on which was dusted finely powdered potassium uranyl sulphate while the varnish was still "tacky." The cell was cylindrical, of glass, with a quartz end, and was filled with a very dilute aqueous solution of uranin, the sodium salt of fluorescein. The end of the cell on which was mounted the quartz window was cut obliquely so that the plane of the window made an angle of about 60° with the axis of the cell. The screen, when used, was placed as shown at F in Fig. 1. The cell, when used, was placed as shown at F' in Fig. 1, with its axis coincident with the optic axis of the lens L_3 and with the quartz window turned obliquely away from the eyepiece E' so that the solution immediately behind the window was viewed through the glass side-wall. The screen gave the more brilliant

image, but the cell was preferable at certain settings where there was appreciable scattered visible light in the field. The maximum intensity of emitted light from both potassium uranyl sulphate and uranin lies at about the same wave-length as the maximum of visual sensitivity for faint illumination. This, together with their intense fluorescence, makes these materials particularly suitable for fluorescent eye pieces.

The whole system was enclosed in a light tight housing, and care was taken to exclude all light from the room. The eyes were rested in total darkness before each set of readings, and it was found possible to set the compensator and analyzer quite sharply to the position of quenching.

The surface cleaning apparatus was the one used by Wheeler,[8] with a few minor refinements. This has been described in detail by him. The mercury used had been electrolytically purified and distilled, and was the purest available. Precautions were taken to avoid contamination, the mercury coming in contact only with glass, "pure gum" rubber tubing, and iron, all of which were carefully cleaned. The mercury pool is shown diagrammatically at *M*, Fig. 1, the surrounding cup, upper and lower mercury reservoirs, etc., being omitted. Simply allowing mercury to run in through the nozzle in the center of the pool and overflow the rim, which was ground to a knife edge, produced an exceedingly clean surface, as shown by the consistency with which readings could be repeated on successive surfaces.

Measurements

The lines of the mercury arc which were used were identified by taking the interval between them from a plate made with a spectrograph of similar dispersing system. The plane of polarization of the polarizing prisms was determined by reflecting light from a distilled water surface at the polarizing angle, the water surface having been cleaned by the method described above for mercury. The divided circles of the prisms were investigated for uniformity of scale. The compensator was calibrated over the full range of motion of its wedge at each wave-length used. The angle of incidence was made 74° 50′, which is close to the principal angles of incidence for mercury at the wave-lengths used, and was checked by two methods. Readings were taken with the polarizer both right and left of the plane of incidence in each series, and at both 0° and 180° quenching points along the full travel of the compensator wedge.

Observations were made in still air quite free from dust, and the mercury surface was cleaned every five minutes, although no change in constants could be detected in a surface standing as long as fifteen minutes. Measurements were repeated to within the probable error of

observation over a period of several months, and it is believed that surfaces were obtained free from all contaminating films, the figures representing absolute values for the metal itself. The temperature of the room and of the mercury remained between 20.0° and 22.0°C throughout the period of observation.

The results obtained, together with the probable errors, are given in Table I and are shown graphically in Fig. 2. The values of n and nk were computed from the formulas given above, and the reflectivity at normal incidence, R, from the formula

$$R=\frac{n^2(1+k^2)+1-2n}{n^2(1+k^2)+1+2n}.$$

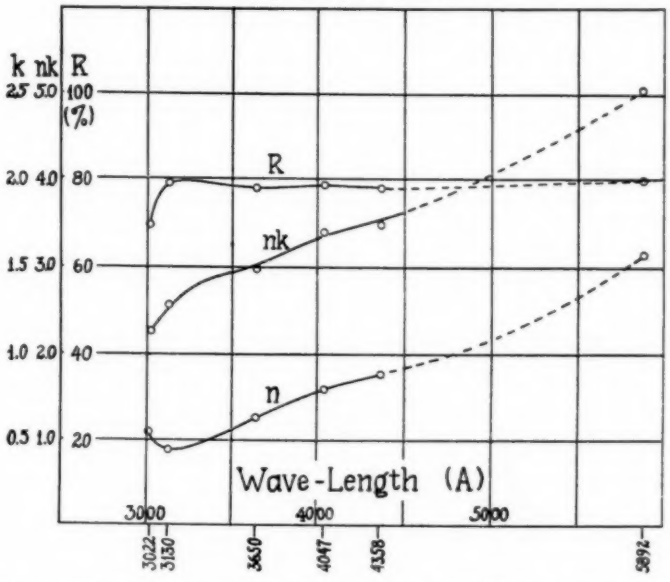

Fig. 2. The optical constants of mercury as a function of wave-length.

The figures in parentheses were computed from values of Q, P, and S, at wave-length 5892A, and for $\varphi=60°$, given by Wheeler.[8] He has also

TABLE I

Optical constants of mercury in air

λ	φ^0	Δ^0	ψ^0	n	nk	R(calc)
(5892A)*	(60.00)	(149.73±0.07)	(40.67±0.09)	(1.57)	(5.05)	(79.6)%
4358	74.83	92.2 ±0.18	38.3±0.09	0.88±0.01	3.47±0.01	77.1±0.4
4047	74.83	90.7 ±0.18	38.9±0.16	0.79±0.03	3.40±0.02	78.5±0.8
3650	74.83	83.3 ±0.15	39.5±0.10	0.64±0.01	2.97±0.01	77.7±0.7
3130	74.83	74.7 ±0.23	40.8±0.12	0.44±0.01	2.53±0.02	78.9±0.9
3022	74.83	69.4 ±0.48	39.4±0.16	0.55±0.01	2.25±0.03	69.7±1.4

* Results for this wave-length are from measurements by Wheeler.[8]

measured[12] the constants of mercury at wave-lengths 5770, 5461, and 4358A. The present result for 4358A is in good agreement with his. Settings were made at wave-length 4047A both by the direct visual method and with the phosphorescent screen, and agree within the probable error.

It is of interest to note from the trend of the curves at the shortest wave-length investigated, that we are apparently approaching a region of transparency similar to that found for silver at slightly longer wave-length.

The writer wishes to thank Professor B. B. Boltwood, from whom the uranium salts and fused silicon were obtained, Dr. G. C. Southworth, whose aid in reading and recording the polarimeter settings greatly increased the accuracy of the experimental work, and Professor Lynde P. Wheeler, at whose suggestion the problem was undertaken and who gave much helpful advice throughout the work.

SLOANE LABORATORY,
YALE UNIVERSITY,
October 22, 1922.

BOOK REVIEWS

Popular Wissenschaftliche Vorlesungen. E. MACH. (Fifth enlarged and revised edition).—This collection of essays dedicated to the memory of Professor William James contains 33 papers which were delivered over a period of over fifty years by Professor Mach. Many of these have been translated and some have appeared in book form. They cover a wide range of subjects but, in the main, are concerned with the philosophical basis of Physics and of Science in general. Mach's philosophy of life is explained in detail and he again emphasizes many of the difficulties in our philosophical approach to Physics. There is not one of them which cannot be read with interest by the teacher of Physics; and those who are familiar with his books on Mechanics and Heat especially will recognize the great influence Mach has had in presenting in logical form the underlying facts of all branches of Physics, and making clear the hypotheses or postulates on which the science rests. Many of his concepts must, of course, be replaced in view of the changes brought into our philosophy by Einstein and others, but this fact does not detract from the importance of his work. Many of the essays deal with the connection between Physics and Psychology, or Physics and psychical phenomena. On the whole Mach's influence as illustrated by these papers is notable and is also of permanent value.—Pp. 628, Johann Barth, Leipzig, 1923. J. S. AMES

Chemistry in modern life. SVANTE AUGUST ARRHENIUS, Director of the Nobel Institute, translated by Clifford S. Leonard, former Fellow in Chemistry of the American Scandinavian Foundation.—Dr. Svante Arrhenius differs from most research men of the first rank in that he is both willing and able to write for the general reader. His theory of the electrolytic dissociation opened a new era in analytical chemistry, and he has been one of the leaders and rewarders of scientific investigation ever since. Yet he does not disdain to talk of "Chemistry in Modern Life" in nontechnical language.

Arrhenius is a humanist in the widest sense of the word, and he is interested alike in the theory and applications of his science, in its history and its everyday uses. His "Chemistry in Modern Life" which proved a popular book in Sweden and Germany, is now published in English as one of the Van Nostrand "Library of Modern Sciences." The translator, Dr. Clifford S. Leonard, who as one of the exchange fellows of the American Scandinavian Foundation worked under Arrhenius in the laboratory of the Nobel Institute in Stockholm, has done more than merely put the book into English words, for he has eliminated some of the material that was of local interest and substituted corresponding references to American chemical industries.

The author has contributed a special preface to the American edition in which he reiterates the warning that he has often voiced before, that the public should realize that the rapid expansion of modern civilization is due to the use of fossil fuels and the easily accessible ores, all of which are limited in amount, and that chemists must study the possibilities of developing new energy sources if our civilization is to be maintained. This pregnant paragraph from his preface is worth quoting entire:

> The material basis of our present civilization depends on the use of fossil fuel. But it has been calculated that the accessible fossil coals will be nearly at an end in about 1,000 years, and petroleum in about twenty years. If we do not find some new source of energy within a thousand years, humanity will fall back to a state of civilization similar to that about a century ago, while the number of inhabitants of our planet will have to diminish to a corresponding degree. Luckily we have the energy of the water-falls which will not diminish in a sensible degree in comprehensible time, unless we cut off the forests

on which the water reserve is more or less dependent. We must harness these falls to save as much as possible of our present material culture. But even when we have taken them into our service they cannot compensate for the loss of fossil fuels. Humanity stands, therefore, before a great problem of finding new raw materials and new sources of energy that shall never become exhausted.

In the end Arrhenius reverts again to the thesis with which he began and concludes with the Chemists' Commandment "Thou shalt not waste."

The volume contains a vast amount of information on industrial processes and the practical meaning of chemical reactions. For instance, the chapter devoted to "The Cultural Value of Silica" covers a wide range from the baked clay of the Stone Age to the recent revolution in architecture due to concrete. Arrhenius does not dodge any of the difficult reactions or technical details in the glass and porcelain industries, but collates his material with skill. He, of course, devotes special attention to "The Sources of Energy" throughout the world, and discusses the possibility of a greater use of wind motors and the invention of solar engines. A greater part of the book is devoted to inorganic chemistry and metallurgy, but the chapters on "Dyes, Perfumes, and Drugs," "Cellulose and Rubber" and "The Bread Question" are practical and interesting.—New York, D. Van Nostrand, 1925. $3.00. EDWIN E. SLOSSON

The Principles of Thermodynamics. GEORGE BIRTWISTLE. The purpose of this book is unusual in a treatise on thermodynamics, namely to sketch the broad general principles and the most important practical applications for such men as intended mathematicians, chemists, astronomers, and physicists, whose future scientific work may be expected to bring them into more or less intimate contact with thermodynamics. The book seems admirably adapted to this purpose. The treatment is simple and the general tone almost conversational. Casual references are made to an immense variety of topics of physical importance, so that the virgin reader must be impressed by the erudition of the author and fascinated by the vista opened to him. If, however, fascinated by this exposition, he decides to make a more serious study of thermodynamics, he will do well to supplement this book with some other in which the conceptual difficulties are more emphasized, and from which a mastery of the difficulties in practical applications may be obtained by the solution of problems.

A quite minor criticism, in which I happen to be personally interested, refers to my experimental determination of the properties of liquids at high pressures; it is said that various thermodynamic relations were "tested" by these experiments. In these experiments no attempt was made to test any thermodynamic formula, but the results of thermodynamics were freely used in making deductions from the data, which were thermodynamically independent.

Subjects not treated, which might well come within the scope of such a book are: the third law of thermodynamics, more extensive reference to applications in physical chemistry, and Saha's work on thermal dissociation in the stars.—Pp. 163, Cambridge University Press, 1925. 7s. 6d. P. W. BRIDGMAN

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY

MINUTES OF THE CHICAGO MEETING, NOVEMBER 27 AND 28, 1925

The 135th meeting of the American Physical Society was held at the Ryerson Physical Laboratory, Chicago, Illinois, on November 27 and 28, 1925. The President of the Society, Professor Dayton C. Miller, presided. Morning and afternoon sessions were held with an attendance of about two hundred. The Saturday morning session was divided into two sections.

On Friday evening the Society held an informal dinner at the Quadrangle Club, attended by sixty-five members and guests.

The regular meeting of the Council was held on Friday, November 27, 1925. The following were elected to membership: Vernon M. Albers, Frank C. Archambo, Jr., Eugene M. Bacigalupi, Carl I. Baker, Roland F. Beers, Norman C. Beese, J. G. Black, E. Bungartz, John F. Burns, Alvin B. Cardwell, R. A. Castleman, Jr., F. M. Clark, Palmer H. Craig, William H. Crew, W. D. Crozier, Richard C. Darnell, Myrl N. Davis, Raymond Davis, F. M. Defandorf, Arthur F. Dittmer, E. Gilbert Dymond, Charles K. Eckels, Paul G. Edwards, Alexander Ellett, W. A. Ellmore, Edgar N. Griscwood, Vernon Guthrie, I. J. Gwinn, Adolph Haberly, Thomas F. Hargitt, Jamison R. Harrison, Gaylord P. Harnwell, K. Horovitz, Arnim D. Hummell, Charles W. Jarvis, T. J. Jones, William J. Jensen, Ernest J. Jones, Varnakale L. Jones, Olaf M. Jordahl, J. P. Karbler, Burton A. Kingsbury, John Kralovek, George G. Kretchmar, John R. Loofbourow, Erwin F. Lowry, Eric R. Lyon, Walter A. MacMair, M. C. Magarian, Miles J. Martin, Harry B. Marvin, L. R. Maxwell, George E. Merritt, Warren W. Mutch, Nathaniel C. Norman, A. Ray Olpin, E. B. Penrod, Donald S. Piston, A. H. Poetker, A. Porilsky, W. E. Ramsey, Alfred M. Randolph, R. A. Rogers, Duane E. Roller, Addison M. Rothrock, II, Leone Sagui, Vesper A. Schlenker, Walter A. Schneider, Raymond S. Seward, H. M. Sharp, George R. Shaw, Henry Shore, Francis G. Slack, Kenneth O. Smith, Henry E. Stauss, Fenton V. Stearns, James D. Stranathan, Paul K. Taylor, Harold C. Urey, Carl P. Utterback, Calvin N. Warfield,

Bertram E. Warren, Wallace Waterfall, Harold E. Way, Julian H. Webb, Harold A. Wheeler, Gerald W. Willard, Thomas S. Wilson, Y. H. Woo, Robert S. Wood, Lawrence H. Yingling.

The regular scientific session consisted of 60 papers (10 of which were read by title), abstracts of which are given on the following pages. An **Author Index** will be found at the end.

HAROLD W. WEBB,
Secretary

ABSTRACTS OF PAPERS

1. Energy distribution between the modified and the unmodified rays in the Compton effect. Y. H. Woo, University of Chicago.—Using small tubes of the Compton type and Soller collimators, reliable measurements of the intensity of the scattered x-rays were obtained from five radiators—paraffin, wood, carbon, aluminium and sulfur. In the case of each of the first four scatterers the Mo Kα rays were scattered at 60°, 75°, 90°, 105°, 120°, 135°, 150° and 165° with the exception that for aluminium no reliable result was obtained at 165°. The scattering with sulfur was observed only at 75°, 90° and 105°. The results show that the energy ratio of the modified to the unmodified line for a given radiator increases with increasing scattering angle, as predicted by Jauncey's theory (Phys. Rev. **25,** 314 and 723); but a comparison of the numerical values of the intensity ratio given by Jauncey for carbon and sulfur at 90° with the present results indicates that the theory overestimates this ratio. Experiments were also performed by keeping a lithium radiator in a lead cell filled with hydrogen. As far as they go, the results indicate that in the secondary x-rays scattered from metallic lithium the unmodified line in the Compton effect disappears.

2. Separation of the modified and unmodified scattering coefficients of x-rays. O. K. DEFOE and G. E. M. JAUNCEY, Washington University, St. Louis.—The methods of a previous paper (Proc. Nat. Acad. Sci., **11,** 517) for measuring the ratio of S_2, the modified scattering coefficient at a given scattering angle ϕ, to S_1, the unmodified scattering coefficient, have been improved. Instead of measuring the scattered intensities entering an ionization chamber set at ϕ before and after the transfer of a certain thickness of aluminum from a position P in the primary beam to a position Q in the scattered beam, we now keep the scattered intensity the same after the transfer as before by allowing more primary rays to fall upon the scattering block. This is done by means of a slit whose opening can be varied. A formula for S_2/S_1 is given in terms of the slit openings before and after the transfer of a known thickness of aluminum from P to Q and of the change of absorption coefficient of the modified rays in aluminum on scattering. A null method has been devised, in which two ionization chambers set at the same angle ϕ at opposite voltages are connected to the same electrometer. Aluminum is transferred from P to Q for one chamber but not for the other.

3. A precision measurement of the change of wave-length of scattered x-rays. H. M. SHARP, University of Chicago.—According to the quantum theory, the change of wave-length of scattered radiation is $\delta\lambda = h/mc\,(1-\cos\phi)$ where h is Planck's radiation constant, m is the mass of the electron, c the velocity of light and ϕ the angle of scattering. A test has been made when ϕ was 169°, using molybdenum radiation and paraffin as the scattering material. The scattered beam passed to a calcite crystal and slit attached to the x-ray tube and thence to the photographic plate. The observed value of $\delta\lambda$ is $(.04825 \pm .00017)$ A and the calculated value $(.04798 \pm .00009)$A. Using the data

of the experiment a value of the *mass of an electron* independent of e/m has been determined. This value is $(8.99 \pm .034) \times 10^{-28}$ g.

4. Theory of the intensity of scattered x-rays. G. E. M. JAUNCEY, Washington University, St. Louis.—The theory of previous papers (Phys. Rev. **25,** 314 and 723) predicts a value for the ratio of s_2, the energy of the modified x-rays scattered at an angle ϕ, to s_1, the energy of the unmodified x-rays. The theoretical value of s_2/s_1, however, is based on the assumption that the probability that an electron will scatter in a direction ϕ when it is in an orbital position M to scatter modified rays, is the same as that when it is in an orbital position U to scatter unmodified rays. This assumption is incorrect and, instead of giving s_2/s_1, the theory gives $p(\phi)$, the fraction of electrons which at any instant are in the M position, and $\{1-p(\phi)\}$ the fraction in the U position. The angular distribution of the intensity of the modified rays is then given by multiplying the right side of Eq. (27) of Compton's paper or of Eq. (21) of Jauncey's paper (Phys. Rev. **21,** 483 and **22,** 233) by $p(\phi)$. However, due to the invalidity of the above assumption, the angular distribution of the intensity of the unmodified rays is not given by multiplying the right sides of the above equations by $\{1-p(\phi).\}$

5. The disappearance of the unmodified line in the Compton effect. G. E. M. JAUNCEY, R. A. BOYD and W. W. NIPPER, Washington University.—Jauncey's theory of the unmodified line (Phys. Rev. **25,** 314) requires the disappearance of this line at values of the scattering angle greater than that given by vers $\phi = 242\ \lambda_0^2/\lambda_s$, where λ_0 is the wave-length of the primary x-rays and λ_s is the K critical absorption limit of the scattering substance and both λ_0 and λ_s are given in angstroms. For the scattering of Mo Kα or Mo Kβ x-rays by carbon or by any element of higher atomic number, there is no real solution of the above equation and the unmodified lines are always present. However, for scattering by boron the unmodified Kα and Kβ lines should disappear at 147° and 117° respectively. We have accordingly scattered Mo x-rays by boron at about 145° to 150° and have examined the scattered spectrum photographically by means of a Sieman-Ross x-ray spectrometer. After a 60 hour exposure the modified Kα and Kβ lines show up plainly but the unmodified lines are either absent or are so faint that they escape detection. Further experiments are in progress.

6. The scattering and absorption of the gamma-rays of radium. H. M. CAVE and J. A. GRAY, Queen's University.—(1) Gamma-rays filtered through 2 cm of lead have a mass scattering coefficient equal to $0.102\ Z/A$, where Z is the atomic number and A the atomic weight of the material used. $(\mu/\rho)_{Pb}$ is 0.053. (2) Gamma-rays for which $(\mu/\rho)_{Pb} = 0.0475$ have been isolated. (3) The distribution of the radiation scattered from paraffin wax has been determined. (4) The results indicate that gamma-rays filtered through 2 cm of lead have an effective wave-length in the neighborhood of 0.012A. It must be stated, however, that the variation of scattering and absorption coefficients with wave-length is not known with sufficient accuracy for an estimation of this wave-length to be made with any degree of certainty.

7. The K series emission spectra for elements from atomic number 50 (Sn) to atomic number 83 (Bi). J. M. CORK and B. R. STEPHENSON, University of Michigan.—Using a spectrograph similar to that previously described except having a greater distance (75.593 cm) between slit and photographic plate, measurements were made upon the K emission spectra of all elements from Sn 50 to Bi 83 inclusive except 54(Xe), 61, 67 (Ho), 75, and 80(Hg). The wave-length values of the α', α, β and γ lines are given in every case except for the γ line of Bi 83. In addition the frequency numbers ν/R and $(\nu/R)^{1/2}$ are given. Variations with atomic number in the value of the regular doublet wave-length difference $d\lambda$ for the α' and α lines, are shown, together with irregularities in some of the outer energy levels of elements in the rare earth group.

8. Theory of the continuous x-ray spectrum. M. SANDOVAL VALLARTA, Massachusetts Institute of Technology.—A theory is presented, based on the following principles: (1) The continuous x-ray spectrum is due solely to stoppage of electrons on the anticathode; (2) emission takes place as light-quanta satisfying Bohr's frequency relation; (3) conservation of energy and of momentum hold for a system made up of impinging electron, anticathode atom and emitted light-quantum; (4) the impinging electron may or may not lose all its kinetic energy (the loss of energy is at random for different electrons); (5) the relation $m=m_0(1-\beta^2)^{-\frac{1}{2}}$ holds for both electrons and atoms; and (6) mass is equal to $h\nu/c^2$. Differences in electron velocities before impact are neglected, also possible changes in the potential energy of atoms. As may be seen, the continuous and the characteristic spectra are supposed to have a different mechanism of emission. One consequence that can be tested experimentally is that the sharp limit depends not only on the tube voltage but also on the direction of observation and on the anticathode material. This has already been pointed out by Bronstein. The effect is measurable only for voltages less than 1 kv and elements lighter than aluminum. Curves are given showing variation of expected effect for different voltages and different materials.

9. Energy distribution in the continuous x-ray spectrum. C. N. WALL, University of Illinois, (introduced by Jakob Kunz).—H. A. Kramers has given a theory which accounts for the main features of the energy distribution in the continuous x-ray spectrum as observed by H. Kuhlenkampff and others. The theory is based upon energy radiation processes which occur in a collision between a free electron and a positive nucleus, and upon ideas underlying Bohr's correspondence principle. In this paper the theory is simplified by considerations of both energy and angular momentum radiation processes which occur during a collision. The result obtained is essentially the same as that obtained by Kramers.

10. Diffraction of x-rays in liquids. G. W. STEWART, ROGER M. MORROW and E. W. SKINNER, University of Iowa.—Using the Kα radiation from a molybdenum target, the diffraction of x-rays was determined by an ionization chamber placed at varying scattering angles θ. The following are the experimental results: *By Morrow*: (a) Solid and liquid camphor at 21°C and 205°C respectively show the same location of intensity peaks, allowance being made for expansion. (b) Naphthalene, α-naphthol and β-naphthol, as liquids, each give a single broad peak which is roughly a mean of the peaks occurring with the solid state. These single broad peaks occur at temperatures close to the freezing point, also crystalline peaks persist to the melting point. *By Skinner*: (a) In each of the five normal saturated alcohols, methyl, propyl, hexyl, octyl and decyl, a single broad peak is accompanied by smaller ones indicating a larger "grating" spacing. The intensity curves are similar but shifted to smaller values of θ with the heavier molecule.—The above experiments are favorable to the interpretation of the phenomena as having an interatomic cause, probably the existence of crystal fragments giving low resolving power. All known data are favorable and none contradictory to this assumption of crystal fragments.

11. Diffraction of x-rays by a ruled metallic grating. R. L. DOAN and A. H. COMPTON, University of Chicago.—X-ray spectra may be obtained by ordinary optical methods if a grating of large constant is used, with sufficiently small glancing angles of incidence. It is necessary to work within the angle of total reflection, in which case the reflected beam is relatively quite intense. The expression for the wave-length is $n\lambda=\frac{1}{2}d(\alpha^2+2\alpha\theta)$ where θ and α are respectively the angles of incidence and diffraction. X-rays from a molybdenum target, made homogeneous by reflection from a calcite crystal, were allowed to fall upon a grating at a glancing angle of less than 10 minutes

of arc. In the best photographs three orders of spectra were obtained. Measurements of wave-length on the $K\alpha_1$ line gave: $\lambda = (0.707 \pm .003)$A. Experiments carried out with a copper tube were hindered by lack of intensity but such calculations as could be made were satisfactory. More precise measurements on the $K\alpha_1$ radiation from these two elements are now in progress.

12. Lattice parameters and densities of Cu, Ag and W. WHEELER P. DAVEY and T. A. WILSON, General Electric Co.—If diffraction patterns of two strain-free crystals are taken on the same film, the crystals have the same equivalent center of diffraction if they are both diluted so as to have the same efficiency of diffraction. A review of diffraction patterns of Cu previously reported showed that this requirement had not been sufficiently met. New patterns have been taken (a) with the calibrating substance (NaCl) mixed with the Cu, and (b) with diluted Cu at one end of the specimen tube and NaCl at the other end. Both methods give 3.605A for the side of the unit cube. This gives a density of 8.95. A single crystal of Cu 3 inches long and 1 inch in diameter gave a density 8.953 by ordinary methods. This changes Patterson's values for Cr and Ti by 0.3 percent. Density measurements by ordinary methods on a large single crystal of Ag gave a density 10.481, agreeing with the previously reported value 10.49 by x-ray methods. New x-ray experiments on W using both methods of calibration confirm the previous result, side of unit-cube = 3.155A; density = 19.32. This value for W is consistent with the new value for Cu.

13. On some solutions of Maxwell-Lorentz equations which may correspond to Bohr's quantum postulates. N. RASHEVSKY, Westinghouse Electric and Manufacturing Company, East Pittsburgh, (introduced by Dayton Ulrey).—It is pointed out that the two postulates of the quantum theory, (1) the existence of accelerated electron motion without radiation, and (2) the emission of monochromatic radiation by a non-periodical motion of the electron, are incompatible not with the classical field equations themselves, but only with their solutions in terms of retarded potential. Using advanced potentials, solutions compatible with (1) have been obtained by G. Nordstrom and Leigh Page. A way of obtaining solutions compatible with (2) has been indicated by Lanzsos for a non-euclidian space. In this paper (a) the general mathematical conditions, which a solution must satisfy in order to be compatible with (1), are investigated; also (b) such a solution is actually constructed by adding to the retarded potentials other suitable chosen solutions of the homogeneous equations; and finally (c) by a similar method solutions are constructed, compatible with (2). It is investigated under what conditions the solution (b) can continuously pass into (c) and vice versa.

14. Transition probabilities and principal quantum numbers. FRANK C. HOYT, University of Chicago.—In calculating approximate values of probabilities of transition from the amplitudes in a harmonic analysis of the electric moment of the atom, the order of the harmonic "corresponding" to a given transition depends on the quantum numbers of the stationary states involved. Hence it would seem possible to determine these quantum numbers in doubtful cases by comparison of such computed values with those deduced from experiment. However, in the case of a single electron moving in an orbit of the penetrating type as in ordinary series spectra it may be shown from the harmonic analysis obtained elsewhere (Phys. Rev. **25**, 174, 1925) for such an orbit that the dependence of the amplitudes on the order of the harmonic is such that they are in reality functions only of quantities that may be found from the energies in the stationary states (effective quantum numbers) alone, together with the subordinate quantum numbers. The transition probabilities are thus independent of the assignment of principal quantum numbers. This question is of importance in view of recent attempts to draw conclusions as to the principal quantum numbers from experiments on the intensities, absorption, dispersion, or magneto-rotation of spectral lines.

15. Stripped oxygen. I. S. BOWEN and R. A. MILLIKAN, California Institute of Technology.—We have heretofore obtained and published the spectra of the stripped atoms of all the elements contained in the first two rows of the periodic table except oxygen and fluorine. We can now report the successful stripping of the oxygen atom and the location of the doublet corresponding to the first term of its principal series at λλ1031.98, 1037.69. The ionization potential is here 137 volts, a number higher than that possessed by any of the atoms thus far stripped, or indeed of any optical series thus far worked upon. We have also obtained the pp' group of the two electron system O_{V}, with such resolution as to clearly bring it out as a sextriplet instead of a quintriplet, and to fix the p_1p_2/p_0p_1 (Sommerfeld notation, Atombau p. 577) ratio for oxygen at 2.27, a ratio fairly close to the value shown by all two-valence-electron systems except beryllium.

16. The pp′ groups in atomic spectra. R. A. SAWYER, University of Michigan.—In order to explain the pp' groups in two-valence-electron systems, Wentzel, and Saunders and Russel have suggested that the second electron makes a ds transition, while Bowen and Millikan favor a ps transition. The present paper suggests as a more general relation that the pp' frequency is associated with the difference in frequency between the two lowest singlet levels in the spectrum concerned and with the difference in level between the two lowest doublet levels in the next spectrum (once more ionized atom). This may be a singlet SP, singlet SD, doublet $\sigma\pi$ or doublet $\sigma\delta$ transition. For certain two-valence-electron system spectra the pp' frequency is nearly a mean between the lowest singlet SP transition and the lowest doublet $\sigma\pi$ transition of the next system. From this relationship the location of the pp' group of ZnI has been predicted and the group identified. For three-valence-electron systems the pp' group is near the lowest singlet SP transition of the next system. The πX doublet of AlI has been identified. Numerical examples are given and the significance of these results discussed.

17. The spectrum of beryllium. R. F. PATON and W. H. SANDERS, University of Illinois.—The comparatively simple structure of the beryllium atom makes its line spectrum a matter of particularly great interest. However, due to its chemical and physical properties the knowledge of its spectrum is very meager. Fortunately the authors were able to secure from Dr. B. S. Hopkins a sample of beryllium-aluminum alloy formed in the preparation of pure beryllium. Samples of this alloy used as electrodes in a vacuum spark chamber, furnished a satisfactory source. The spectrum was photographed with a quartz spectrograph. Several satisfactory spectrograms have been obtained and the results tabulated from λ5200 to λ2000. The known lines of beryllium are the most intense on the plates. In addition to these there is a considerable number of new lines which have been ascribed to beryllium, since they occur on all the beryllium plates, but correspond to no recorded wave-lengths and are absent from spectrograms of impurities. More complete data now being taken should permit the classification of these new beryllium lines in series.

18. The absorption spectrum of manganese vapor. R. V. ZUMSTEIN, National Research Fellow, University of Michigan.—By heating the manganese in a small carbon tube to about 1600°C, absorption was observed at 31 lines. Grotrian had reported absorption at 6 lines. All of the absorptions are from manganese atoms in the normal state (1^6s term) and occur in groups of 1, 2 and 3 lines. Five absorption lines represent $1^6s-{}^6d'$ combinations for which the rule of inner quantum numbers is obeyed but the azimuthal quantum number changes by 2. Four lines are $1^6s-{}^5p$ combinations and twelve are $1^6s-{}^6p$ combinations. Some of the remainder are perhaps $1^6s-{}^4p$ and $1^6s-{}^2p$ combinations.

19. The Zeeman effect for the spectrum of flourine. G. HOWARD CARRAGAN, University of Chicago.—An electromagnet suitable for work on the Zeeman effect at high

field strengths has been designed and constructed for the purpose of this investigation. Certain improvements in the technique of handling flourine have been instituted and a form of discharge tube has been devised which is suitable for giving the flourine spectrum under high field strengths. The red spectrum has been photographed in the 1st, 2nd and 4th orders of the 10-inch Michelson grating, and the Zeeman patterns of twenty of the brighter lines obtained. The analysis of these patterns with a consideration of the ratios of the intervals between the lines and the distribution of their relative intensities seem to indicate a quartet system. The principal and diffuse series term combinations have been located on this basis. The term combinations of other lines have been proposed and certain unexplained anomalies in the spectrum pointed out. Certain lines observed by Gale and Monk but not given in their published list of wave-lengths are cited.

20. The law of force and the size of diatomic molecules, as determined from their band spectra. RAYMOND T. BIRGE, University of California.—Assuming for the law of force of a diatomic molecule, in the vicinity of the equilibrium position, $F=k_1(r-r_0)+k_2(r-r_0)^2+$ etc., explicit expressions for the k's have been derived in terms of the constants of the usual *rotational* energy function for a *non-vibrating* molecule, $E_m=Bm^2+Dm^4+Fm^6$ etc., where m is generally a half integer. Values for the k's, from the *vibrational* energy function of a *non-rotating* molecule may be obtained from the work of Born and Hückel. Although the error is much greater when using rotational data, the two independent values of k_1 are found to agree on an average to two percent, for the initial and final states of the CN, CuH, N_2 and N_2^+ molecules. Dieke's explanation of the intensity anomalies of non-polar molecules requires a moment of inertia I only one-quarter as large as the older accepted values, and this in turn makes the value of k_1, from rotation only, just four times as large. Hence the above quantitative agreements, based on the older values of I, form conclusive evidence in favor of these older values.

21. The quantum analysis of the band spectrum of AlO (λ5200-λ4650). W. C. POMEROY and R. T. BIRGE, University of California.—Using a new form of aluminum arc, spectrograms were taken in 1915 by one of us, in the second order of the large concave grating of the University of Wisconsin. These have now been measured and the (0,0), (1,0), and (0,1) bands of the blue and green group analyzed according to the quantum theory. Although the series lines of each band are concealed in the vicinity of the "origin," these points have been definitely located by an extensive and accurate verification of the combination principle. No other choice of origins gives even approximate verification. The necessary theoretical relations between vibrational and rotational energy constants enable the absolute values of the rotational quantum numbers to be established to ± 0.02. They are exact half-integers. The origin of the (0,0) band (λ4842) is at $\nu_{vac}=20{,}635.3$, and the limiting values of the moments of inertia for initial (emission) and final states are $(46.01\pm0.04)\times10^{-40}$ and $(43.38\pm0.04)\times10^{-40}$ respectively. These bands have no Q branch, and the P and R branches consist of doublets of the violet CN type. The three bands measured have no observable perturbations. Additional theoretical relations are now being tested.

22. Effect of the type of source on the primary standard of wave-length. GEORGE S. MONK, University of Chicago.—Owing to its use as the primary standard of wave-length, it is of fundamental importance to know under what conditions of production, if any, the wave-length of the red Cd line 6438.4696 A, will vary. Accordingly, several sources have been studied by the use of the Fabry-Perot etalon and auxiliary grating dispersion. In agreement with the determinations of Hamy it is found that the electrodeless tube yields the same value as one with electrodes. The design of the tube and the type of discharge have no observed effect on the wave-length. The cadmium-filled carbon arc in

vacuum gives the same value, but owing to greater intrinsic line width, the measurements from this source are attended by a larger error. Also, some interesting differences in intensity have been observed. The strongest visible line in the sharp singlet series, λ5154, is subject to measurements of the highest order of accuracy, but on account of its relative faintness is not desirable as a standard of wave-length.

23. Greater dispersion in the extreme ultra-violet. R. J. LANG and STANLEY SMITH, University of Alberta, (introduced by G. W. Stewart).—The construction and operation of an optical *vacuum-grating spectrograph* capable of accommodating a grating of two meters radius of curvature is described. Means are provided for introducing and removing the photographic plate as well as for altering the focus and inclination of the grating while the vacuum is maintained. *Doublet separations for* C_{II}. The following doublets in Fowler's series have been resolved. For $(2\pi_{1,2}-3\sigma)$, $\Delta\nu=64$ in the second order of the grating and 60 in the third order. For $(2\pi_{1,2}-3\delta)$, $\Delta\nu=64.5$ in 2nd order. For lines $\lambda=1335$ $\Delta\nu=65$ and lines $\lambda=1036$, $\Delta\nu=62$ showing that since the 1036 line belongs to C^+ probably 1335 does also. *Doublet separation for* Si_{III}. In this series the doublet $(3\sigma_{1,2}-4\pi)$ has a separation $\Delta\nu=153$.

24. Coloring of glass in ultra-violet light. C. L. CROSS, University of Iowa, (introduced by John A. Eldridge).—It is known that glasses containing manganese are tinted when subjected to x-ray or radioactive illumination and that the same phenomenon occurs when the glass is subjected to ultra-violet light. The phenomenon is closely related to phosphorescence. It is found that the effective light has a wave-length only slightly greater than 2900 (the absorption limit of the glass). Consequently the tinting is confined to very near the surface. The tinting is greatly hastened by heating. Two different colors may be obtained depending on temperature. At room temperature a brown color is produced which with time turns to purple. At 100°C the purple is produced at once. The reverse action (decolorizing) is accelerated by heat or visible light. A possible mechanism is suggested.

25. The passage of protons and charged hydrogen molecules through gases. A. J. DEMPSTER, University of Chicago.—Protons and charged hydrogen molecules with a slow velocity, corresponding to a potential difference of 300 to 900 volts, will pass through many molecules without being neutralized, contrary to what would be expected from the results with canal rays and α rays. Thus protons have been observed with their original charge after 9 collisions with hydrogen and 26 collisions with helium atoms, using the kinetic theory value of the molecular diameters. The rays were still observable, though scattered, when the number of collisions was four times as great as that just mentioned. Similar results hold in the case of charged hydrogen molecules. In air and hydrogen the penetration is somewhat less and the scattering greater. The velocities of the rays are small compared with the orbital velocity of the electrons, so that we may think of the rays as causing only an adiabatic distortion of the electronic arrangement while passing through, and producing no permanent alteration in the electronic distribution. There is no tendency for the helium to give up an electron since its ionization potential is 24.5 volts, and the energy of formation of the neutral atom or molecule considerably less.

26. Collisions of the second kind in activated ozone. H. D. SMYTH, Princeton University.—Last February a report was made concerning some experiments on collisions of the second kind between electrons and pseudo-excited atoms in iodine. Extension of the ideas on which that work was based suggests that if an electron collides with an activated molecule, the energy of activation or "critical increment" of the molecule may be converted to kinetic energy of the electron by a collision of the second kind, the

molecule, of course, being thereby reduced to a normal state. Experiments have been made on ozone decomposing into oxygen. With a simple arrangement of filament, grid, and plate, the current reaching the plate was measured as a function of a retarding field between the plate and grid. A constant small accelerating field was maintained between the filament and grid. If the process suggested above does occur, there should have been some electrons that had greater velocity than that due to the accelerating field alone, and such electrons should have been able to reach the plate after the retarding field was sufficient to cut off the main group. Some evidence of such high speed electrons was obtained.

27. Critical ionization potentials by positive ion impact in hydrogen. W. J. HOOPER, University of California.—The experiments of several previous investigators were repeated in substance with apparatus designed to make it possible to distinguish between ionization and certain spurious factors which have made questionable much of the existing evidence relating to ionization by positive ion impact. A great many current-potential measurements and curves were obtained with a variety of electrical arrangements. The data and curves thus obtained present direct evidence (a) that the previously so-called ionization current is due to a secondary electron emission from the walls of the ionization chamber and not to ionization of the gas, (b) that this secondary electron emission is produced by the impact of the positive ions against these metal walls, (c) that either there is no ionization in hydrogen gas by the impact of positive ions accelerated by potential differences up to 925 volts, or that if this phenomenon exists, its effects are so small at relatively low pressures (.012 mm) that it is completely masked by secondary phenomena which make its detection by the ordinary direct methods problematic, and (d) that it seems possible that at relatively high gas pressures, ionization by positive ions might be an important factor with accelerating potential differences well within this same range of voltages.

28. An optical and electric study of the striated discharge in alkali vapors. A. J. MCMASTER, University of Illinois.—A study of the low voltage discharge in potassium vapor using a hot cathode of oxide-coated platinum wire is being made. When a small quantity of hydrogen is admitted to the discharge tube, beautiful striations of more than one color are produced. The distribution of the potential in and between the striations is measured by the exploring electrode according to the space charge method of Langmuir. A striation exhibits a number of well defined layers of different colors which are investigated by the spectroscope.

29. The distribution of potential in low voltage arcs. O. S. DUFFENDACK and W. S. KIMBALL, University of Michigan.—Langmuir's sheath method was employed in measuring the distribution of potential in low-voltage arcs in hydrogen. The space a millimeter away from the filament is at practically the same potential as the anode. Thus there is a large fall of potential very near the cathode and only a small potential gradient over the remaining space. Only two potential states seem possible for a particular tube, a pre-arc state and an arc state. An oscillating arc is one in which there are rapid transitions between these two states. When a sufficient potential difference is applied between filament and anode of a soft detector or gas filled tube, an arc will strike unless the grid is made negative with respect to the filament; then an arc will not strike until the potential difference between the grid and filament is reduced to a characteristic value. After the arc strikes it becomes independent of the grid potential over wide limits. Such tubes have been used for locking circuits at critical instants and for peak voltmeters. After the grid potential reaches the critical value, an arc strikes in a very short time (order of one ten thousandth second) which becomes less with increasing anode potential.

30. Low-voltage characteristic in mercury vapor. RICHARD RUDY, Nela Research Laboratory.—The low-voltage mercury arc studied is produced between a surface of mercury and tungsten ribbons 1 to 2 mm wide and 1 to 3 cm long. As the electron emission is increased, the characteristic is gradually shifted towards lower voltages, and the arc finally becomes an abnormal low-voltage arc. Increasing the temperature of the ribbon lowers the voltage of the arc until strong currents pass at voltages lower than the first excitation potential. No oscillations are observed, since the characteristic is rising. Reverse fields may exist in the ordinary as well as in the abnormal low-voltage arc. These have been investigated by measuring the resistance of the arc by means of superimposed high frequency currents. With moderate heating of the filament the saturation current is well marked and is followed by a linear increase in current with the voltage, as ionization again sets in. The slope of this straight line is nearly proportional to the saturation current. With strong electron emission the ionization masks the saturation current. Currents of over half an ampere are possible with the anode less positive than the positive end of the filament. The effect of argon on this low voltage arc has also been examined.

31. Studies on active nitrogen. RICHARD RUDY, Nela Research Laboratory.—Afterglow was produced in a bulb containing nitrogen at a few mm pressure by passing a momentary discharge through the bulb. The rate of decay of the afterglow increased with increasing nitrogen pressure, so that the total light emitted became smaller and smaller. This effect was of the same order as the extinction of fluorescence in mercury when the density is increased. Argon, up to a few cm pressure, had little influence on the rate of decay. The decay was found to follow a bimolecular law for the first 100 seconds. The temperature coefficient of this reaction, between 20° and 130°, is much smaller than that of ordinary chemical reactions. For a bright afterglow all the bands of the first positive group of nitrogen were observed. In a bulb about 20 cm in diameter, afterglows lasting more than 15 minutes were obtained. The nitrogen molecule retains vibrational energy and therefore reacts quickly with other substances, or causes them to emit light, as if at high temperature. Band spectra excited by active nitrogen (particularly if the vibrational quanta are not too different) show vibrational energy as if at high temperature, whereas the rotational energy indicates low temperature.

32. On the discharge of electricity between equipotential plates. MASON E. HUFFORD, Indiana University.—A study has been made of the glow discharge of electricity between a perforated cathode and a connected auxiliary electrode. The dependence of the presence of the discharge upon pressure range was determined with aluminum electrode and various gases, air, oxygen-coal-gas, hydrogen-coal-gas, oxygen, hydrogen and helium. Experiments showed that electrons are evolved from the metal surface behind the cathode and these neutralize the canal rays. Experiments were made to show the relation of total voltage on the discharge tube to the current from cathode and auxiliary plate. Potentials at points in the glow region were measured by the probe method. The change of potential of a fixed point in the glow with change of pressure was tested. Study was made of the glow potentials using copper as cathode and again using gold as cathode. Potentials were measured when the walls of the tube were coated with sputtered metal and the discharge consisted of a glow only. Comparison was made of the fall of potential in the glow region and the cathode fall of potential obtained by other experimenters.

33. Mobility of the ions in the corona discharge. W. M. YOUNG, University of Illinois, (introduced by Jakob Kunz).—The mobilities of the ions generated in the direct current corona discharge have been directly measured. Gas, moving with a uniform velocity, has been ionized in a cylindrical corona tube and then passed into an ion chamber consisting of a hollow cylinder with electrodes along the axis. The ion current

to the last electrode, when plotted as a function of the cylinder potential, exhibited maxima which indicated the formation of groups of ions. A large number of groups were obtained whose mobilities, for oxygen, nitrogen, and carbon dioxide were all less than .716 cm/sec/volt/cm, ranging down to 10^{-5} cm/sec/volt/cm. Nearly all mobilities were found less than 10^{-2}, the ions apparently being generated in about equal numbers, except that now and then a greater number of a certain mobility were formed. If it can be assumed that the charge determines the mobility of the ion, evidence can be found of ions which contain different charges. However, if mass is the determining factor, then ions may be picked out having the same charge but whose mobility varies inversely as the square root of the molecular weight. The fact that the ions all possessed small mobilities seems to indicate that J. Kunz made the correct assumptions when he calculated the average value from the experimental determination of the pressure increase in the d.c. corona.

34. Geiger counting chambers. C. W. HEWLETT, General Electric Co.—A study of Geiger counting chambers has been made, with the object of throwing some light on the mechanism by which radioactive rays register themselves in this type of apparatus. Evidence has been obtained suggesting that, in order to be registered, a radioactive ray must pass through a conical region extending from the point to the walls of the chamber. The extent of the base of this conical region may be very small and located on the end closing the chamber, or it may be large, covering the whole end of the chamber and even part of the side walls, depending upon the distance of the point from the end of the chamber. Examples are given of the determination of small amounts of radioactive matter mixed in relatively large amounts of other matter.

35. Shot-effect of electrons produced by impact ionization. ALBERT W. HULL and N. H. WILLIAMS, General Electric Company.—A two-electrode tube with pure tungsten filament was filled with argon to a pressure of .04 mm. The temperature of the filament was adjusted to give .003 m-amp. emission and the plate voltage raised until this emission current was multiplied thirty fold by ionization, giving a total current of 0.1 m-amp. The shot-effect was found to be exactly the same as for pure temperature-limited electron emission. This result would be in harmony with the hypothesis that ionization is effected in two steps, namely, absorption of energy from the impinging electron by the atom as a whole and subsequent emission of an electron after a brief, but random, interval. Such a process would account for the observation of Dushman and Found (Phys. Rev. **23,** 734, 1924) that the ionization in different gases is proportional to the total number of electrons in the molecules of the gases. A much larger shot-effect would be expected on the conventional theory of instantaneous emission, which assumes two low velocity electrons leaving the atom together as the result of an ionizing collision. It is possible, however, that some modification of this theory could account for the observed result.

36. The "reflection" of electrons from the anode of a Coolidge x-ray tube. W. R. HAM and MARSH W. WHITE, Pennsylvania State College.—Some of the electrons impinging on the anode of an x-ray tube are "reflected" to other portions of the tube. The ratio of the number reflected to the total number was measured quantitatively and found to be surprisingly large. The method employed was to measure the energy input into a water-cooled tube from a d.c. source and the heat received at the anode. The latter was obtained by using a flow calorimeter method. In a previous paper (Phys. Rev. **23,** 777, 1924) the writers described experiments which proved the equivalence between the energy input into an x-ray tube and the heat which is ultimately produced. Consequently the fraction of the electrons which are reflected is the ratio of the difference between the total energy and the heat generated at the target to the total energy input. The data indicate that the percentage of reflected electrons rises from approximately 15 at 2 kv to

25 at 5 kv and then falls off to 13 at 20 kv. These data were taken with a current of 10 m-amp. The experiments are being continued to study the variation of the reflection coefficient with other factors.

37. The role of the Faraday cylinder in the measurement of the velocities of the electrons emerging from small apertures. ERNEST O. LAWRENCE, National Research Fellow, Yale University.—The experiments of Lehmann and Osgood (Proc. Cam. Phil. Soc., **22,** 731) led to the conclusion that a large fraction of the electrons emerging from small apertures have velocities less than the velocity corresponding to the applied voltage. However, the efficiency of the Faraday cylinder was not experimentally investigated. Present experiments with a Faraday cylinder of variable dimensions have shown that the observed apparent lack of homogeneity of velocities of the electrons is very definitely a function of the cylinder, indicating that a considerable part of the apparent inhomogeneity is merely due to a re-emission of electrons from the cylinder. These experiments show that Faraday cylinders in general are not as efficient absorbers as is usually assumed. This conclusion is further illustrated by the experiments of J. T. Tate (Phys. Rev. **17,** 395, 1921) who found that the most efficient Faraday cylinder he designed had an absorption coefficient of about .95.

38. Thermionic work function and space charge. J. SLEPIAN, Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pa.—Work function and space charge are separated on the basis that work function is microscopic in nature and space charge macroscopic. The work function then varies with electron space density, becoming zero or negative if the electron space density is sufficiently high. For an electrode in contact with a completely ionized gas at atmospheric pressure, the work function is reduced by about 0.6 volt.

39. Thermionic and evaporation characteristics of adsorbed films of caesium on tungsten. J. A. BECKER, Bell Telephone Laboratories, Inc.—When a tungsten filament in caesium vapor is heated above a critical temperature T_c of 800°K, every atom that strikes evaporates as a positive ion. When the temperature T is lowered to 600° K, the caesium deposits, the electron current increases, comes to a sharp maximum at t_m seconds, decreases and later becomes steady. This shows that a certain number N_0 of caesium atoms produce an optimum activity. If the initial $T > T_c$ and the final $T < 600°$, t_m depends only on the positive ion current i_p. Hence above T_c the filament is bare if we draw positive ions; and below 600°K every atom that strikes sticks, at least until N_0 have stuck. If i_p is changed by varying the bulb temperature, $i_p \times t_m$ remains constant. From the value of this constant, $N_0 = (3.9 \pm .2) \times 10^{14}$ atoms/cm², which indicates that at the optimum the caesium is closely packed and has its atomic rather than its ionic diameter. Varying the initial conditions before lowering T shows that if the plate is negative both atoms and ions evaporate, while if it is positive only atoms evaporate. The atomic rate of evaporation increases with the fraction of the surface covered, whereas the ionic rate decreases.

40. Emission of positive ions from hot tungsten filaments. R. L. KENWORTHY, University of Iowa, (introduced by John A. Eldridge).—Jenkins has shown that when the filament of a Coolidge tube is made very hot, positive ions are emitted. If heated for some time with reversed potential (which kept the positives from leaving the filament), the available positive ions appeared to accumulate so that when later an attracting field was applied an abnormally large positive emission was observed for several minutes. Using a special two element tube the phenomenon was further studied. In general Jenkins' results were confirmed. It was found that the proportion of the evaporated atoms which carried a positive charge was 1 in 1600.

41. Investigation of photo-electric valve coated with potassium. V. M. ALBERS, University of Illinois.—The tube used by Tykociner and Kunz has been studied more thoroughly. In the case of a transparent deposit on the connecting tube, curves are given showing the current through the tube when illuminated, I_l, and when dark, I_d. The ratio I_l/I_d reached a minimum at 40 and at 300 volts. The difference reached a maximum for a potential difference of 200 volts. The current increased linearly with light intensity at first and then less rapidly, approaching a saturation value. With an opaque film of potassium, illuminated through a window, the current increased in proportion to the voltage to 1000 volts and also in proportion to the light intensity. Evidently the thicker film gave the more efficient valve. Tests with dispersed light showed that with both transparent and opaque films, the current per unit energy decreased rapidly with increasing wave-length, reaching zero at between 520 and 540 $m\mu$. In explanation of these effects it is suggested that photo-electric emission from the film reduces the accumulation of electrons on the wall which tends to stop the current through the tube by electro-static repulsion. However, this does not explain the variation of the effect with wave-length.

42. The electrical conductance of the halides of sodium. T. E. PHIPPS, W. D. LANSING, and T. G. COOKE, University of Illinois, (introduced by Jakob Kunz).—The electrical conductance of the halides of sodium in the solid state was measured over a wide range of temperature. The powdered crystals were compressed under high pressure to semitransparent disks. In the case of NaCl, the conductance of this disk agreed very well with that of a natural crystal. A relation between conductance and temperature was derived theoretically and found to be $\kappa = ce^{-\epsilon/kT}$, where κ is the conductance, and ϵ is the energy of liberation of an ion in the lattice. Then $\epsilon = -kd \log \kappa/d(1/T)$ and ϵ can be calculated from the slope of the log κ, $1/T$ curve. Experimentally, each salt showed two distinct slopes, that at higher temperatures being approximately twice that at lower temperatures. A tentative explanation suggested for this behavior is that the positive ion alone conducts at lower temperatures and both ions at higher temperatures. It was found that for each sodium halide the energy of liberation of an ion in the lower temperature range was approximately 39 times the natural quantum of the crystal as derived from specific heat data.

43. Measurements of high frequency amplification with shielded-grid pliotrons. ALBERT W. HULL, General Electric Company.—Further tests have been made with the tubes previously described (abstract, Phys. Rev. **23,** 299, 1924). The distinguishing feature of these tubes is that they are made as nearly unidirectional as possible by thorough electrostatic shielding between the control-grid and plate. The shielding is accomplished internally by means of an extra grid between control-grid and plate, maintained at a constant positive potential, and externally by appropriate arrangement of supporting and leading-in wires and the use of grounded conductors. In this way it was found possible to reduce the effective capacity between control-grid and plate to less than .01 e.s.u. The most interesting application of these tubes is voltage amplification at high frequencies. Amplification measurements were made at 50, 1,000, and 10,000 kilocycles. At 50 kc the voltage amplification per stage was 200. At 1,000 kc each tube amplified 40-fold, and 4 in series gave a total voltage amplification of 2 million. This is shown to be the maximum amplification that can be usefully employed at any frequency, because of the presence of shot-effect. At 10,000 kc each tube amplified 7-fold, and 5 in series gave 10,000. No oscillations or other evidences of feedback were observed at any frequency. The use of *negative plate resistance* was found to be advantageous for cascade amplification with low battery voltage, and for single tube operation.

44. Measurement of the series resistance of a condenser at radio frequency. CHARLES D. CALLIS, Indiana University, (introduced by R. R. Ramsey).—The variable

condenser is placed in a radio frequency (10^6 cycles) circuit with a coil made of fine wire with approximately the same high frequency and d.c. resistance. The resistance of the circuit is measured by the well known resistance variation method. The resistance is then measured with a second coil exactly like the first replacing it, and again with the two coils placed in series opposition so as to have the same inductance as that of one coil. From these three readings the resistance of the coils and the resistance of the condenser can be determined. It is found when the coils are made of fine wire that the computed resistance of the coils is the same as their d.c. resistance. Since the computed resistance is the d.c. resistance the assumption is made that the resistance of the coils is independent of position and constant, and that the computed resistance of the condenser is the true resistance. A number of sets of coils were made in order to obtain the condenser resistance at various dial readings. These values plotted against the reciprocal of the capacity give approximately a straight line.

45. The high frequency resistance of condensers in series. R. R. RAMSEY, Indiana University.—In attempting to get a check on the work of Charles D. Callis (preceding abstract) it was discovered that if two condensers of the same general type were placed in series in a resonant circuit the resistance of the two condensers in series was approximately the same as the resistance of a single condenser when placed in the same resonant circuit. This is found to be a direct consequence of the ordinary law of resistances in series if the resistance of a variable condenser varies inversely with the capacity of the condenser.

46. Linear amplification of galvanometer deflection by the photo-electric cell. F. E. NULL, University of Illinois.—Dr. Jakob Kunz suggested a method whereby the deflection of a moving mirror system may be amplified linearly by reflecting a beam of light from the mirror to a triangular slit in front of a photo-electric cell. This method has the advantage that the photo-electric cell has no lag. It may therefore be used to secure linear amplification of even short period instruments, such as the siphon recorder used in ocean cable signal reception.

47. Electricity and Newton's third law of motion. JOHN A. ELDRIDGE, University of Iowa.—Newton assumes action at a distance and asserts that the action and reaction act in opposite directions on the same line. The "magnetic forces" between two neighboring conductors violate this law, having parallel but not coincident lines of action. The contradiction is in part only apparent because "magnetic forces" are not strictly forces. The terminology is unfortunate since it misleads the student. The actual forces between two charged masses moving in a plane are always in this plane. Insofar as they are directed along the *line joining* the centers of charge they accord with Newton but there is usually a component in the *direction of motion* which is not Newtonian. This situation is usually summarized by saying that the electrical field is not derivable from a potential. While not agreeing with Newtonian mechanics, electrical phenomena are of course in good accord with relativity mechanics.

48. The role of magnetism in valence. E. H. WILLIAMS, University of Illinois.—The formation of chemical bonds by electric forces is difficult to reconcile with the Bohr atom. It has been suggested that valence may be due to magnetic forces produced by electronic orbits. The *magnetic susceptibility of odd and even molecules* (molecules containing an odd or an even number of electrons) has now been measured. Four substances containing both odd and even molecules have been tested. Two of these substances, compounds of copper and chlorine, changed from paramagnetic for odd molecules to diamagnetic for even molecules and the other two, compounds of manganese and cobalt, while strongly paramagnetic for odd molecules, became less paramagnetic for even molecules. This was especially noticeable in the case of cobalt compounds which de-

creased more than ten fold. Two oxides of both tin and lead were also examined. Since the atomic numbers of both of these el ments are even, the oxides form even molecules. In all four cases the substances were diamagnetic. While conclusions cannot be drawn from the limited number of substances worked with, it is interesting to note that in all cases substances that are weakly paramagnetic for odd molecules become diamagnetic for even molecules and substances that are strongly paramagnetic for odd molecules become less paramagnetic for even molecules.

49. Temperature coefficient of magnetic permeability of sheet steel. THOMAS SPOONER, Westinghouse Research Laboratory, East Pittsburgh.—The temperature coefficients of magnetic permeability as a function of maximum induction and maximum magnetizing force are given for commercial sheet steel such as is used in electrical apparatus. The temperature range is from $-20°C$ to $+46°C$. Three grades of material were tested having a silicon content of approximately 0.9, 2.2 and 4 percent, respectively. The average temperature coefficients have a negative sign for all inductions for the high silicon steel but for the low and medium silicon steels the coefficients are positive for the low inductions and negative for the high. The maximum negative temperature coefficients occur at about 10 kilogauss, which is appreciably higher than the inductions corresponding to maximum permeability.

50. J. W. Fisher's experiments and the possibility of magnetization by rotary fields. S. J. BARNETT, Carnegie Institution of Washington and California Institute of Technology.—In two recent investigations, with negative results, J. W. Fisher has looked for longitudinal magnetization of ferromagnetic cylinders in a cross magnetic field rotating in a plane normal to their axes. The present paper criticizes Fisher's theory, showing that the magnetization calculated by him should be multiplied by a factor approximately three halves the ratio of the cross magnetization to the saturation magnetization, thus reducing it very greatly and making the effect, if existent, undetectable under his experimental conditions. Another investigation of this effect, which is closely related to that of magnetization by rotation, now long established, is in progress here. A magnetic field, approximately uniform throughout a certain toroidal region and with intensity normal to the generating circles of the toroid, is produced and rotated by a two-phase current system. The toroid is filled with a ring, circular in cross-section, of fine permalloy wire surrounded with symmetrical coils in circuit with a galvanometer, whose throw is read when the rotation is reversed. This arrangement takes full advantage of permalloy's enormous susceptibility and eliminates disturbances due to fluctuations of the earth's field; and it is hoped that the elimination of other disturbances will make a conclusive investigation of the effect possible.

51. Torque on revolving cylindrical magnet. A. L. KIMBALL, JR., General Electric Co.—In a paper recently published in the Physical Review by Zeleny and Page, it was shown that the explanation often given of the cause of electromagnetic rotation of a cylindrical magnet with a side arm dipping into an annular trough is incorrect, but that by taking account of the reaction between the flux and current both in the magnet and in the side arm a good check between experiment and theory can be obtained. In the present paper it is shown that the experiment can also be explained by regarding the torque as arising from the reaction between the current in the part of the circuit external to the magnet, and the magnetic field, thus avoiding the necessity of thinking of the torque as arising from a reaction between current and field *both* carried by the suspended magnet, as assumed by Zeleny and Page. Both theories lead to the same law of torque.

52. The vapor pressure of solid sodium amalgams. FRANKLIN E. POINDEXTER, Washington University, St. Louis.—A Buckley ionization gauge was used to measure

the vapor pressure of eight sodium amalgams ranging in concentration from 1:1 to 15:1 mol ratio of Hg to Na. The vapor pressure of each amalgam was measured at a number of temperatures which were determined by means of a platinum resistance thermometer. The pressures measured varied from approximately 10^{-8} mm to 10^{-3} mm over a maximum temperature range of from $-56°$ to 90°C. The log p vs $1/T$ graphs for the different amalgams were found to be approximately straight lines. The heats of reaction were calculated by means of the Van't Hoff reaction isochore, the pressures at different temperatures for these calculations being taken from the log p vs $1/T$ graphs. These heats of reaction varied from 15000 cal. in the case of the amalgams rich in Hg to 14,000 cal. for the 2:1 amalgam. This small heat difference over such a wide range of concentrations indicates that most of the heat of reaction between Na and Hg is liberated in the formation of the initial compounds.

53. Variation of the coefficient of viscosity of air with the relative humidity. J. C. STEARNS, University of Chicago, (introduced by H. G. Gale).—The coefficient of viscosity of air with various relative humidities was measured by the concentric cylinder method. The presence of water vapor decreased the viscosity at all pressures. At atmospheric pressure the viscosity was reduced one third percent by saturating the air. At a pressure of 14 mm, the viscosity was reduced by 35 percent of its value when moisture was introduced.

54. Transmission of sound by masonry partitions. PAUL E. SABINE, Riverbank Laboratories.—The reduction of the intensity of sound in transmission from room to room by way of partition walls of masonry was measured by the reverberation method. Eighteen tones, covering the pitch range from 128 to 4096/sec. were employed. Tests were made on walls 50 square feet in area, built into a doorway between two rooms entirely separated structurally. Eighteen walls, including the common types of permanent partitions were tested. The structural stiffness of the partitions was also determined by measuring the yielding of the mid-point under a small excess of atmospheric pressure on one side. For a single tone, the results of the tests were not interpretable. The average reduction over the whole tone range, however, proved to be independent of the structural stiffness of the partition and of the particular material employed and to be a function only of the mass per unit area of the partition considered as a whole. For masonry partitions under the test conditions ranging in weight from 10 to 45 pounds per square foot, the reduction of sound intensity in transmission is given very approximately by the equation $I/i = .593$ (Wt. in pounds/Area in sq. ft.).[5/2]

55. Transmission of sound by double-wall partitions. PAUL E. SABINE, Riverbank Laboratories.—The average reduction of intensity of sound in transmission by a single wall of gypsum tile was measured over the frequency range, 128 to 4096/sec. A second wall of the same weight and material was built without any structural connection and with an intervening air space of 2 inches between the two walls. The effects of structurally bridging and of filling this space with different materials were determined by measuring the transmission of sound by these structures. The following ratios of intensities, upon opposite sides of various composite walls of this type were obtained: single wall, 420; double wall bridged with wood, 10,300; double wall, sawdust filled, 8,700; double wall, slag filled, 11,300; double wall, felt filled, 31,000; double wall, completely separated and without filling, 32,000. The conclusion is drawn that the bridging action of a filler of absorbent material more than offsets the reduction of acoustical energy due to absorption by such a material.

56. The action of acoustic wave-filters in solids. H. F. OLSON, University of Iowa, (introduced by G. W. Stewart).—Quantitative measurements of transmission in solid filters composed of brass cylindrical masses attached to a brass rod conduit, have been

made, and those in which the branches are cylindrical masses of like diameters and lengths show the following results. The application of the formula for low-frequency-pass filters in fluids was found possible provided the inertance of the branch is made equal to 0.75 of the volume and the capacitance of the branch 8.5×10^{-13} of the volume. The increase in volume of the branch, the increase in distance between the branches, and the appearance of the additional bands are all in accordance with the formulas for low-frequency-pass-filters. The physical action of the filter is very complicated but the above empirical relations indicate that a simplified theory of the action can be secured.

57. Optimum reverberation in auditoriums. F. R. WATSON, University of Illinois.—One of the necessary considerations in designing or correcting the acoustics of an auditorium is to secure conditions that will insure an optimum time of reverberation. A number of publications have dealt with this question, but from somewhat different standpoints. The writer has attempted to discuss these results on a common basis to show any differences that may exist.

58. Anomalous action of the Rayleigh disk. CHARLES H. SKINNER, Ohio Wesleyan University.—The turning moment on a Rayleigh disk when used to compare sound intensities is usually considered as proportional to the intensity and in such a direction as to set the disk more nearly at right angles to the axis of the resonator in which the disk is mounted. For certain short wave-lengths, however, the turning moment is reversed, and the disk tends to take up a position parallel to the axis of the resonator. The longest wave-length for which this occurs is approximately two times the diameter of the disk, the exact value depending on the relative dimensions of the disk and resonator.

59. The practical importance of relativity. JOHN A. ELDRIDGE, University of Iowa.—The restricted theory of relativity is usually considered recondite, without *practical* application. It is true that Newtonian mechanics are sufficiently accurate in other engineering applications, but not in the field of magnetism the existence of which is an indication of the breakdown of classical mechanics. In an electrical age it is hardly possible to consider relativity as an impractical refinement upon the Newtonian mechanics.

60. The isotopic composition and the atomic weight of terrestrial and meteoric chlorine. WILLIAM D. HARKINS and S. B. STONE, University of Chicago.—Accurate determinations of the atomic weights of meteoric and terrestrial chlorine indicate that this element has the same isotopic composition in the meteorite as on earth, which is favorable to the hypothesis of Harkins that the percentage of isotopes in elements is determined at least largely by the relative stability of the different types of atoms. The average atomic weight on earth of the meteorites is found by these determinations to be 35.457_6, which indicates 77.13 percent of the light isotope and 22.87 percent of the heavy, provided the atomic weights of the separate species are exactly 35 and 37. The table listed below gives in parentheses the number of determinations and the values represent the ratio of silver-chloride to silver, found by direct weighing, with the probable errors calculated by the method of least squares.

(7)	Apatite	1.32867_4	±	0.0000033
(7)	Wernerite	1.32867_4	±	43
(7)	Hydrochloric acid	1.32867_4	±	43
(21)	Terrestrial	1.32867_4	±	31
(7)	Meteoric	1.32868_0	±	47
(28)	Meteoric and terrestrial	1.32867_6	±	23
(8)	Sodalite	1.32868_9	±	67

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